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TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

ABBREVIATED TITLE.	JOURNAL.
A.	Abstracts in Journal of the Chemical Society.*
Amer. Chem. J.	American Chemical Journal.
Amer. J. Physiol.	American Journal of Physiology.
Amer. J. Sci.	American Journal of Science.
Analyst	The Analyst.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Chim. anal.	Annales de Chimie analytique appliquée à l'Industrie à l'Agriculture, à la Pharmacie et à la Biologie.
Ann. Falsif.	Annales des Falsifications.
Ann. of Botany	Annals of Botany.
Ann. Physik	Annalen der Physik.
Ann. Report	Annual Reports of the Chemical Society.
Apoth. Zeit.	Apotheker Zeitung.
Arch. expt. Path. Pharm.	Archiv. für experimentelle Pathologie und Pharmakologie.
Arch. Hygiene	Archiv für Hygiene.
Arch. Néerland	Archives Néelandaises des sciences exactes et naturelles.
Arch. Pharm.	Archiv der Pharmazie.
Arch. Sci. phys. nat.	Archives des Sciences physiques et naturelles.
Atti R. Accad. Sci. Torino.	Atti della Reale Accademia delle Scienze di Torino.
Atti R. Accad. Lincei	Atti della Reale Accademia dei Lincei.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
Ber. Deut. bot. Ges.	Berichte der Deutschen botanischen Gesellschaft.
Ber. Deut. pharm. Ges.	Berichte der Deutschen pharmazeutischen Gesellschaft.
Ber. Deut. physikal. Ges.	Berichte der Deutschen physikalischen Gesellschaft.
Bio-Chem. J.	The Bio-Chemical Journal.
Biochem. Zeitsch.	Biochemische Zeitschrift.
Boll. chim. farm.	Bollettino chimico farmaceutico.
Bull. Acad. roy. Belg.	Academie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. Acad. Sci. Cracow	Bulletin international de l'Académie des Sciences de Cracovie.
Bull. Acad. Sci., St. Pétersbourg	Bulletin de l'Academie Impériale des Sciences de St. Pétersbourg.
Bull. Assoc. Chim. Sucr. Dist.	Bulletin de l'Association des chimistes de Sucrerie et de Distillerie.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Bull. Soc. chim. Belg.	Bulletin de la Société chimique de Belgique.
Bull. Soc. franç. Min.	Bulletin de la Société française de Minéralogie.
Centr. Bakt. Par.	Centralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.
Centr. Min.	Centralblatt für Mineralogie, Geologie und Palaeontologie.
Chem. News	Chemical News.
Chem. Weekblad	Chemisch Weekblad.
Chem. Zeit.	Chemiker Zeitung.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Gazzetta	Gazzetta chimica italiana.
J. Agric. Sci.	Journal of Agricultural Science.

* The year is not inserted in references to 1910.

ABBREVIATED TITLE.	JOURNAL.
Jahrb. Min.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
Jahrb. Min. Beil-Bd.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie. Beilage-Band.
Jahrb. Radioaktiv. Elektronik	Jahrbuch der Radioaktivität und Elektronik.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Biol. Chem.	Journal of Biological Chemistry, New York.
J. Chim. phys.	Journal de Chimie physique.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Iron and Steel Inst.	Journal of the Iron and Steel Institute.
J. Landw.	Journal für Landwirtschaft.
J. Path. Bact.	Journal of Pathology and Bacteriology.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Physical Chem.	Journal of Physical Chemistry.
J. Physiol.	Journal of Physiology.
J. pr. Chem.	Journal für praktische Chemie.
J. Roy. Soc. New South Wales	Journal of the Royal Society of New South Wales.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
Landw. Jahrb.	Landwirtschaftliche Jahrbücher.
Landw. Versuchs-Stat.	Die landwirtschaftlichen Versuchs-Stationen.
Mem. Coll. Sci. Eng., Kyōtō	Memoirs of the College of Science and Engineering, Kyōtō Imperial University.
Mem. Manchester Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Milchw. Zentr.	Milchwirtschaftliches Zentralblatt.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Pflüger's Archiv	Archiv für die gesammte Physiologie des Menschen und der Thiere.
Pharm. Weekblad	Pharmaceutisch Weekblad.
Pharm. Zeit.	Pharmazeutische Zeitung.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).
Physikal. Zeitsch.	Physikalische Zeitschrift.
Proc.	Proceedings of the Chemical Society.
Proc. Amer. Acad.	Proceedings of the American Academy.
Proc. Amer. Physiol. Soc.	Proceedings of the American Physiological Society.
Proc. Camb. Phil. Soc.	Proceedings of the Cambridge Philosophical Society.
Proc. K. Akad. Wetensch. Amsterdam.	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
Proc. Physiol. Soc.	Proceedings of the Physiological Society.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.
Quart. J. Geol. Soc.	Quarterly Journal of the Geological Society.
Rend. Accad. Sci. Fis. Mat. Napoli	Rendiconto dell' Accademia delle Sienze Fisiche e Matematiche-Napoli.
Sci. Proc. Roy. Dubl. Soc.	Scientific Proceedings of the Royal Dublin Society.
Sitzungsber. K. Akad. Wiss. Berlin.	Sitzungsberichte der Königlich Preussischen Akademie der Wissenschaften zu Berlin.
Tech. Quart.	Technology Quarterly.
Trans.	Transactions of the Chemical Society.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Trans. Roy. Soc. Canada	Transactions of the Royal Society of Canada.
Tsch. Min. Mitt.	Tschermak's Mineralogische Mitteilungen.
Zeitsch. anal. Chem.	Zeitschrift für analytische Chemie.

Abbreviated Title.	Journal.
Zeitsch. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeitsch. anorg. Chem.	Zeitschrift für anorganische Chemie.
Zeitsch. Chem. Ind. Kolloide.	Zeitschrift für Chemie und Industrie der Kolloide.
Zeitsch. Elektrochem.	Zeitschrift für Elektrochemie.
Zeitsch. Kryst. Min.	Zeitschrift für Krystallographie und Mineralogie.
Zeitsch. Nahr. Genussm	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Zeitsch. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeitsch. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Zeitsch. Schiess. und Sprengstoffwesen	Zeitschrift für das Schiess- und Sprengstoffwesen.
Zeitsch. Ver. deut. Zuckerind.	Zeitschrift des Vereins der deutschen Zucker-Industrie.
Zeitsch. wiss. Photochem.	Zeitschrift für wissenschaftliche Photographie, Photophysik und Photochemie.
Zentr. Physiol.	Zentralblatt für Physiologie.

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GENERAL AND PHYSICAL CHEMISTRY.

As in the case of previous reports, no attempt has been made to describe the whole of the work carried out during the year under review. The number of subjects dealt with in the report is relatively small; several subjects in which important work is in progress have been held over for fuller treatment at a later date; other investigations, which are now referred to for the first time, are described in such a way as to link up the work of the past year with that of the years immediately preceding.

Ice, Water, and Steam.

The investigations of Tammann [1] on the various forms of ice have been extended [2] to the recognition of four distinct varieties, two of which, "Ice I" and "Ice IV," are lighter than water, whilst the other two, "Ice III" and "Ice II," are denser; in accordance with his theory of the constitution of water, the denser varieties are regarded as composed of simpler, and the lighter varieties of more complex, molecules; the less stable varieties, IV and II, are regarded as mere polymorphs of the more stable varieties I and III. The triple point for "Ice I," "Ice III," and water is at $-22°$ and 2200 kg./cm.². The freezing point of "Ice I" at different pressures has been redetermined as follows:

$t=$	$-5·53°$	$-7·46°$	$-9·75°$	$-10·42°$	$-12·74°$	$-15·66°$	
$p=$	675	859	1099	1141	1353	1597	kg./cm.²;

at pressures greater than 2200 kg./cm.², the denser "Ice III" is the stable form, but spontaneous crystallisation usually results in the separation of "Ice I" in a metastable form at all pressures up

[1] *Ann. Report*, 1909, 2.

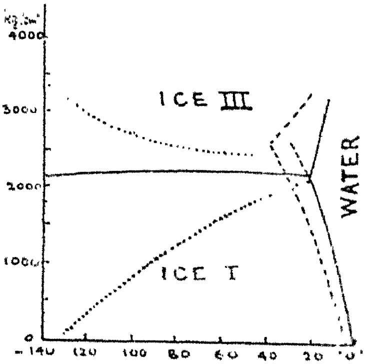
[2] G. Tammann, *Zeitsch. physikal. Chem.*, 1910, **72**, 609; *A.*, ii, 495.

to 2600 kg./cm.², giving rise to a prolongation of the freezing-point curve as follows:

$t =$	$-22{\cdot}0°$	$-25{\cdot}6°$	$-27{\cdot}0°$	
$p =$	2200	2440	2585	kg./cm.².

This extended curve of metastable equilibrium and the two super-saturation curves are shown by broken lines in the diagram. It may be noted that, whilst water under moderate pressures expands when frozen, the contrary effect is produced when the pressure exceeds 2600 kg./cm.², owing to the production of "Ice III" in place of "Ice I"; the maximum pressure produced by freezing water in a bomb cannot therefore exceed 2600 kg./cm.².

At temperatures below $-22°$ the pressures at which "Ice I" passes into "Ice III" are slightly less than 2200 kg./cm.², but the difference is not great; there is, however, a considerable range of pressures above and below the equilibrium-pressure over which



"Ice I" and "Ice III" respectively can exist in a metastable condition. The limits of the metastable condition are well defined, and are indicated by dotted lines in the diagram. It will be noticed that the highest temperature at which the dense "Ice III" can persist at atmospheric pressure is $-130°$; above this temperature it crumbles into a powder of the bulky "Ice I."

"Ice II" resembles "Ice III" very closely. Whereas "Ice III" is formed by compressing to 3000 kg./cm.², and cooling to $-80°$ and then to $-180°$, "Ice II" is formed by cooling first to $-80°$, then compressing to 2700 kg./cm.², and finally cooling with liquid air. When the pressure is wholly or partly released, it is found to revert to "Ice I" at precisely the same temperatures as in the case of "Ice II"; for example, at atmospheric pressures it crumbles to "Ice I" at $-130°$; the triple point for "Ice II," "Ice I," and "Liquid" is at $-22{\cdot}4°$ and 2230 kg./cm.², differing only to a minute extent from the corresponding figures for "Ice III."

"Ice IV" was discovered in plotting the melting-point curve of ice formed by spontaneous crystallisation under pressures from 500 to 2000 kilograms. The melting point was indicated by a sudden decrease of the pressure-readings shown by the manometer, but a premature decrease was frequently observed, followed by a reversion to the original pressure, and a permanent decrease due to the melting of "Ice I" in the normal way. This double change was attributed to the production by spontaneous crystallisation of a less stable "Ice IV," which melted a degree or so below the melting point of "Ice I," froze spontaneously to "Ice I," and then melted at the usual melting temperature. "Ice IV" is perhaps identical with the tetragonal ice observed by E. Nordenskiöld,[3] or with the regular ice crystals which are formed by crystallisation from 75 per cent. alcoholic solutions[4]; it is formed on three occasions out of four when water crystallises spontaneously under moderate pressures in the absence of nuclei of "Ice I."

In addition to the four crystalline varieties of ice described by Tammann, an amorphous or glassy form has been prepared by cooling saturated solutions of certain salts by means of liquid air[5]; somewhat similar results are obtained when water itself is mixed with liquid air, but in this case the glassy condition is less stable, and the water finally solidifies to a turbid, porous mass.[6] Amorphous or colloidal ice can also be prepared by cooling a saturated solution of water in ether by means of liquid air; the opalescent suspension of amorphous ice in ether crystallises or coagulates on warming, giving rise to a flocculent precipitate of ice; when chloroform is used instead of ether, and the cooling is extended only to $-20°$, it is found that colloidal suspensions are produced with greater readiness and are much more stable when substances, such as salts of the higher fatty acids, caoutchouc, colophony, or mastic, are added.[7]

Tammann's observations (which have been extended also to the light and dense varieties of crystalline phenol)[8] can be accounted for by the existence of two varieties of water-molecules, namely, hydrol H_2O ("Ice III and II"), and dihydrol H_4O_2 ("Ice I and IV"). This simple hypothesis, however, is not adequate to explain the properties of liquid water, which appears to be a ternary mixture of a dense compound, perhaps dihydrol H_4O_2, with two lighter compounds, one of which is produced in increasing quantities when

[3] *Pogg. Ann.*, 1861, **114**, 612.

[4] H. P. Barendrecht, *Zeitsch. physikal. Chem.*, 1896, **20**, 240; *A.*, 1896, ii, 417.

[5] P. P. von Weimarn, *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 226; *A.*, ii, 404.

[6] *Ibid.*, p. 230; *A.*, ii, 404.

[7] P. P. von Weimarn and Wo. Ostwald, *Zeitsch. Chem. Ind. Kolloide*, 1910, **6**, 181; *A.*, ii, 400.

[8] *Zeitsch. physikal. Chem.*, 1910, **75**, 75; *A.*, ii, 1051.

the liquid is cooled and is perhaps trihydrol H_6O_3, whilst the other is produced in increasing quantities when the liquid is heated and is perhaps identical with hydrol or steam H_2O. Evidence that less dense varieties of water-molecules are formed both by heating and by cooling has been afforded by the study of the solution volumes of hygroscopic salts dissolved in water, whereby it has been shown that the contraction due to the formation of hydrates (conversion of free water into hydrate-water) increases from a minimum at 30° to 40° whether the temperature be raised or lowered.[9]

It has been shown by E. Bose[10] that the high density of steam[11] can be accounted for most readily by assuming it to contain double and simple molecules in equilibrium, $H_4O_2 \rightleftharpoons 2H_2O$, the dissociation constant being given by the formula $\log K = -4857 \cdot 1/T + 21455$. Assuming that the same constant may be applied to liquid water at corresponding temperatures, the following values for the molecular association of the liquid may be deduced[12]:

	Dissociation coefficient of H_4O_2 in steam.	Association factor of H_2O in water.	Association factor from surface-tension.
80°	0·913	1·90	2·07
100	0·911	1·86	1·96
120	0·910	1·82	1·85

The values thus deduced are fairly close to those derived from surface-tension measurements by means of the formula of P. Dutoit and P. Mojoïu,[13] and shown in the last column. They indicate that the coefficient of association of water, which is definitely lower than 2 at temperatures above the boiling point, rises above this value at temperatures only a little below the boiling point. These values cannot be explained either by Tammann's theory that liquid water is a mixture of H_4O_2 and H_2O, or by Sutherland's theory that water is a mixture of H_6O_3 and H_4O_2, but are in accord with the view that the liquid is a ternary mixture of ice-molecules, H_6O_3, water-molecules, H_4O_2, and steam-molecules, H_2O, in proportions varying with the temperature.

The association coefficient of water in solution has been found to be as follows[14]:

Bromoform	1·05 to 1·30	*p*-Toluidine	1·04 to 1·35
Ethylene bromide	1·18 to 1·29	Methyl oxalate	1·14 to 1·99
Dimethylaniline	1·23 to 1·32	Methyl succinate	1·18 to 1·80
Veratrole	0·98 to 1·67		

[9] Bousfield and Lowry, *Trans. Faraday Soc.*, 1910, **6**, 85; *A.*, ii, 842.
[10] *Zeitsch. Elektrochem*, 1908, **14**, 269; *A.*, 1908, ii, 577.
[11] Kornatz, *Diss.*, Königsberg, 1908.
[12] P. A. Guye, *Trans. Faraday Soc.*, 1910, **6**, 78; *A.*, ii, 841.
[13] *J. Chim. Phys.*, 1909, **7**, 169; *A.*, 1909, ii, 470.
[14] G. Bruni and M. Amadori, *Gazzetta*, 1910, **40**, ii, 1; *A.*, ii, 948.

It was found that alcohol and acetic acid, dissolved in veratrole, also gave normal molecular weights in dilute solutions, but were polymerised when the concentration was increased; phenol and alcohol in ethylene bromide showed a normal molecular weight at the lowest dilutions, whilst acetic acid gave high values throughout; phenol in methyl succinate gave almost normal values throughout, whilst alcohol and acetic acid became polymerised with increasing concentration, although at a much slower rate than in the case of water.

Cryoscopy.

Cryoscopic measurements at low temperatures continue to furnish interesting results. E. Beckmann and P. Waentig[15] have replaced the pentane thermometer by a platinum resistance thermometer for measurements between $-20°$ and $-120°$, and have determined the cryoscopic constants for eight solvents:

	Freezing point.	Cryoscopic constant.	Latent heat of vap. in cal.
Carbon tetrachloride	−24°	298·0	4·17
Pyridine	40	49·7	21·8
Chloroform	61	46·8	46·8
Ether..........................	117	17·9	27·4
Hydrogen iodide	51	202·6	4·31
,, bromide	86	94·1	7·44
,, chloride	112	49·8	10·3
,, sulphide	82·9	38·3	18·8

Alcohols were found to be polymerised in carbon tetrachloride and in chloroform, but to have normal molecular weights in ether. Ketones dissolved in hydrogen iodide were polymerised and gave conducting solutions, probably owing to the formation of complexes such as that observed by McIntosh and Archibald[16] in the case of acetone, namely, $2C_3H_6O,HI$. Hydrogen sulphide, on the other hand, did not give conducting solutions.

Iodine, which, when dissolved in pyridine, gave brown solutions corresponding in molecular weight with the formula I_2, has itself been used as a cryoscopic solvent[17]; the cryoscopic constant is taken as 213, but polymerisation is very marked, even at low concentrations of the solute, and electrolytes resemble organic solutes in being polymerised instead of dissociated. Sulphur at concentrations from 0·89 to 2·36 per cent. gives molecular weights corresponding with the formula S_8, but dilute solutions give lower values. Phosphoryl chloride (m. p. 1·25°, constant 76·8) and bromoform (constant 144) have been used as cryoscopic solvents by Walden.[18]

[15] *Zeitsch. anorg. Chem.*, 1910, **67**, 17; *A.*, ii, 581.

[16] *Trans.*, 1904, **85**, 919.

[17] F. Olivari, *Atti R. Accad. Lincei*, 1909, [v], **18**, ii, 384; **19**, i, 488; *A.*, ii, 18, 582.

[18] *Zeitsch. anorg. Chem.*, 1910, **68**, 307; *A.*, ii, 1036.

Complete freezing-point curves have shown the existence of the compounds $MeOH,NH_3$ and Me_2O,NH_3,[19] corresponding with the hydrate H_2O,NH_3 described in last year's report (p. 14). Chlorine and sulphur dioxide, which melt at $-100{\cdot}45°$ and $-75{\cdot}6°$ respectively, give a eutectic point at $-102{\cdot}3°$, but do not combine to form a crystalline compound; the freezing point is raised, however, by exposure to light, owing to the formation of sulphuryl chloride.[20] Ethyl bromide combines with bromine to form the compound $2C_2H_5Br,Br_2$ prior to giving ethylene bromide.[21] Ethyl ether and ethyl iodide form at least three compounds, probably of the oxonium type, namely, $3EtI,OEt_2$, $2EtI,OEt_2$, and EtI,OEt_2; anisole and benzyl chloride give four compounds, the additional member of the series having the formula $3C_7H_7Cl,2MeOPh$. The freezing point of the ether was found to be $-112{\cdot}1°$,[22] in agreement with Ladenberg and Krügel ($-112{\cdot}6°$), but not with Olszewski ($-117{\cdot}4°$), Guttmann ($-117{\cdot}6°$), or Beckmann and Waentig ($-117°$).

Liquid Crystals.

The discovery that crystalline structure could exist in fluids was a logical sequel to well-known facts in reference to the flow which takes place in crystalline metals when subjected to a pressure varying according to the nature of the metal. The phenomenon of flow under pressure was demonstrated some years ago by Adams in the somewhat extreme case of marble, whilst the observations of O. Lehmann[23] on the "flowing together and healing of soft crystals" of potassium oleate provided an excellent example of the lower limits of crystalline rigidity. The large group of "anisotropic fluids" or "liquid-crystals," of which cholesteryl benzoate,[24] azoxyanisole, and *p*-azoxyphenetole[25] were amongst the first to be discovered, are characterised by a complete fluidity; the orienting power of the molecules is here less effective than surface tension in determining the form of the substances, and a slight opalescence is the only feature which distinguishes them from ordinary liquids so far as their general appearance is concerned. A remarkable proof of the crystalline nature of these fluids was supplied by D. Vörlander[26]

[19] G. Baume and F. L. Perrot, *Compt. rend.*, 1910, **151**, 528; *A.*, ii, 825.
[20] A. Smits and W. J. de Mooy, *Proc. K. Akad. Wetensch. Amsterdam*, 1910, **13**, 339; *A.*, ii, 1049.
[21] A. Wroczynski and P. A. Guye, *J. Chim. Phys.*, 1910, **8**, 189; *A.*, ii, 699.
[22] D. E. Tsakalotos and P. A. Guye, *ibid.*, 340; *A.*, ii, 826.
[23] *Zeitsch. physikal. Chem.*, 1895, **18**, 91; *A.*, 1896, ii, 160.
[24] F. Reinitzer, *Monatsh.*, 1888, **9**, 421; *A.*, 1888, 1076; O. Lehmann, *Zeitsch. physikal. Chem.*, 1889, **4**, 468; *A.*, 1890, 105.
[25] O. Lehmann, *Ann. Phys. Chem.*, 1890, [iii], **40**, 401; **41**, 525; *A.*, 1891, 249.
[26] *Zeitsch. physikal. Chem.*, 1906, **57**, 357, see especially figs. 7 and 8; *A.*, 1907, ii, 70.

in the case of azoxybromocinnamic ester, which, when suspended in a little bromonaphthalene, gives rise to minute droplets with straight edges and sharp angles in which the crystalline form is unmistakable, in spite of the fact that the material is still completely liquid. Such cases are, however, exceptional, and in the majority of the 200 substances of this type that have now been examined,[27] the anisotropic character of the liquid has been deduced from its optical properties, rather than from its mechanical or geometrical qualities. Excellent illustrations of the appearance of liquid crystals, when viewed as thin films under the microscope between crossed Nicol prisms, are given by Vorländer [28] in the paper referred to above.

Although it has been suggested by Tammann [29] and others that liquid crystals are two-phase systems somewhat of the character of emulsions, it has not been found possible to separate them into two constituents by means of electrostatic [30, 31] or centrifugal forces, and their homogeneity is now generally recognised.[32] Nearly all the essential qualities of crystals, with the exception of those which depend on elasticity, have now been detected in crystalline liquids. Well-marked transition-temperatures mark the limits of stability of the liquid-crystalline state, separating it from the liquid state, which is stable at higher temperatures, and the solid-crystal state, which is stable at lower temperatures. These transition-temperatures are lowered by the presence of foreign substances, and the transition from the liquid to the liquid-crystalline state can be made use of in cryoscopic work in just the same way as the transition from liquid to solid; on account of the small thermal changes which accompany the transition, the molecular depression reaches an extremely high value, for instance, in the case of *p*-azoxyanisole (transition-temperatures 116° and 135·2°) as solvent, and quinol or benzophenone as solute, the molecular depression is 4900, corresponding with a latent heat of 0·68 cal. only.[33] By mixing two sub-

[27] See, for instance, D. Vorländer, *Ber.*, 1906, **39**, 803; *A.*, 1906, i, 317.

[28] *Zeitsch. physikal. Chem.*, 1906, **57**, 357; *A.*, 1907, ii, 70; figs. 1 to 6.

[29] *Ann. Physik*, 1901, [iv], **4**, 524; 1902, **8**, 103; 1906, **19**, 421; *A.*, 1901, ii, 231; 1902, ii, 445; 1906, ii, 220.

[30] G. Bredig and G. von Schukowsky, *Ber.*, 1904, **37**, 3419; *A.*, 1904, ii, 714.

[31] A. Coehn, *Zeitsch. Elektrochem.*, 1904, **10**, 856; *A.*, 1905, ii, 14.

[32] See R. Schenck, *Ann. Physik*, 1902, [iv], **9**, 1053; *A.*, 1903, ii, 137, for further arguments based on the abrupt change of properties at the "clearing-temperature" or melting point of the liquid crystals and the substantial constancy of the opalescence over the whole range of temperature over which the liquid crystal persists. For liquid crystals which are not opalescent, see D. Vorländer, *Ber.*, 1908, **31**, 2033; *A.*, 1908, i, 641. For the segregation of impurities during the formation of liquid crystals from isotropic liquids, see O. Lehmann (*Physikal. Zeitsch.*, 1910, **11**, 44; *A.*, ii, 134).

[33] C. de Kock, *Zeitsch. physikal. Chem.*, 1904, **48**, 129; *A.*, 1904, ii, 548. Compare R. Schenck, *ibid.*, 1898 **25**, 337; *A.*, 1898, ii, 286.

stances of this type, a definite eutectic point may be observed, at which two kinds of liquid-crystal separate together from an isotropic liquid, for instance, *p*-azoxyanisole and *p*-methoxycinnamic acid at 107—108° instead of at 135·2° and 185·5° respectively.[34] Cases have also been recorded of substances which may appear in two solid and one liquid-crystalline form,[35] or in one solid and two liquid-crystalline forms,[36] the polymorphism in each case being of much the same character as when all the forms are solid; in the extreme case of ethyl *p*-azocinnamate, not less than three liquid and three solid phases have been observed.[37] Supersaturation and other related phenomena of metastable equilibrium are frequently observed in dealing with liquid crystals,[38] but metastable liquid crystals can often be rendered stable by the addition of a second substance of this type[39]—a phenomenon which resembles closely the isodimorphism of solid crystals.

A complete case of isodimorphism, in which one form of each substance is a liquid crystal, has been discovered in the case of *p*-azoxyphenetole and *p*-azophenetole.[40] The former substance melts at 136·9°, and clears at 167·5°; the latter substance melts at 160·2°, the clearing point of the metastable (monotropic) liquid-crystalline form lying 4° below at 156·1°. In mixtures of the two substances, both the melting point and the clearing point vary with composition according to a linear law, the two lines intersecting one another (at 80 per cent. of phenetole and 156°) on account of the interchange in the relative positions of the melting point and clearing point in the two substances. Melting-point and clearing-point curves are given for eleven other binary mixtures. It is noteworthy that the clearing point lies below the melting point in each of the six azo-compounds that were examined, the liquid-crystalline phase being monotropic (always metastable), whilst in the corresponding azoxy-compounds it is enantiotropic (stable over a definite range of temperature above the melting point).

The viscosity of the crystalline is usually less than that of the isotropic liquid.[41] The flow of crystalline liquids through capillary

[34] C. de Kock, *loc. cit.*

[35] D. Vorländer, *Zeitsch. physikal. Chem.*, 1906, **57**, 357; *A.*, 1907, ii, 70.

[36] D. Vorländer, *loc. cit.*; O. Lehmann, *Zeitsch. physikal. Chem.*, 1906, **56**, 750; *A.*, 1906, ii, 836.

[37] D. Vorländer, *Ber.*, 1907, **40**, 1415; *A.*, 1907, ii, 337.

[38] O. Lehmann, *Ann. Physik*, 1890, [iv], **41**, 535; *A.*, 1891, 249.

[39] O. Lehmann, *ibid.*, 1906, [iv], **21**, 181; *A.*, 1906, ii, 837.

[40] A. D. Bogojawlensky and N. Winogradoff, *Zeitsch. physikal. Chem.*, 1907, **60**, 433; compare also 1908, **64**, 229; *A.*, 1907, ii, 844; 1908, ii, 809.

[41] L. Pucciante, *Atti R. Accad. Lincei*, 1907, [v], **16**, i, 754; *A.*, 1907, ii, 533. Compare and contrast R. Schenck, *Zeitsch. physikal. Chem.*, 1898, **27**, 169; *A.*, 1898, ii, 563.

tubes under moderate pressures presents certain anomalies, which vanish when the head is sufficiently great to produce an eddying or swirling flow in the tube; this phenomenon is regarded by E. Bose [42] as evidence in support of the view that anisotropic liquids are made up of molecular aggregates in which the molecules are arranged in such a way that they tend to move by preference in certain definite directions.

In its solvent power for carbon dioxide, the liquid-crystalline form of *p*-azoxyphenetole is intermediate between the solid, in which the gas is insoluble, and the liquid, which dissolves 26 parts of gas as compared with 18 parts for the liquid crystal.[42a]

Great progress has been made during recent months in the study of the optical properties of liquid crystals, especially in the direction of quantitative measurements. The majority of liquid crystals are uniaxial, the double refraction being positive in sign, as in the case of quartz. A particularly good example is afforded by ammonium oleate,[47] a substance the stability of which in the liquid-crystalline form may be greatly increased by the addition of the isomorphous potassium or sodium salt.[43] A drop of the liquid-crystalline ammonium salt, compressed between a microscope slide and a cover-slip, appears turbid and polarises irregularly; if, however, the cover-slip is tapped with a needle, the liquid becomes clear and gives rise to a perfect uniaxial figure, with black cross. A list of sixteen uniaxial liquid crystals with positive double refraction has been given by Vorländer,[44] together with two illustrations of the interference figures produced in convergent polarised light. An example of negative double-refraction (as in calcite) has recently been described by E. Dorn [45] in the case of cholesteryl propionate.[46] Two biaxial types of crystal (with double refraction weakly negative and strongly positive respectively) are developed when ammonium oleate is cooled below the transition-temperature of the liquid-crystal form,[47] but this type of symmetry is very rare in the liquid-crystalline state; an example has, however, been found in the case of no less familiar a substance than azoxyanisole [48]; the orientation of the liquid-crystals differs according as they are prepared by heating the solid or by cooling the liquid, and two different views can thus be obtained of the coloured lemniscates and hyperbolic brushes.

[42] *Physikal. Zeitsch.*, 1909, **10**, 32 ; *A.*, 1909, ii, 215.
[42a] I. F. Homfray, *Trans.*, 1910, **97**, 1669.
[43] O. Lehmann, *Ann. Physik*, 1906, [iv], **21**, 181 ; *A.*, 1906, ii, 837.
[44] *Ber.*, 1908, **41**, 2033 ; *A.*, 1908, i, 641.
[45] *Physikal. Zeitsch.*, 1910, **11**, 777 ; *A.*, ii, 809.
[46] Compare F. Wallerant, *Compt. rend.*, 1906, **143**, 605 ; *A.*, 1906, ii, 837.
[47] F. Wallerant, *ibid.*, 694 ; *A.*, 1906, ii, 838.
[48] F. Wallerant, *ibid.*, 1909, **148**, 1291 ; *A.*, 1909, ii, 529.

Liquid crystals belonging to the regular system have not yet been discovered; in the absence of double refraction, their existence could only be demonstrated by mechanical or geometrical properties, such as an abrupt change of viscosity with rising temperature or the formation of straight-edged droplets, that is, by methods of investigation that are, as a rule, only applied after the existence of the liquid-crystalline state has been demonstrated by optical examination.

Quantitative measurements of the refractive indices of liquid crystals for the ordinary and extraordinary rays were attempted by O. Lehmann by suspension in a medium of equal refractive power,[49] and by observations of Newton's rings with parallel-polarised light,[50] but the opalescence of the substances chosen did not permit of accurate measurements. Two clear and transparent crystalline liquids discovered by D. Vorländer and W. Kasten [51] have provided material for accurate measurements by a total reflection method (the substance being enclosed as a film between two prisms of suitable angle), and also by observations of Newton's rings with convergent polarised light.[52] The substances studied were ethyl benzylideneamino-α-methyl- and α-ethyl-cinnamate, each being capable of existing in one solid, two liquid-crystalline, and an isotropic liquid form. The methyl compound melts at 95° to a liquid-crystal I and passes at 125° to an isotropic liquid; when this is cooled it reverts to liquid-crystal I at 125°, but further cooling results in the production (at 76°) of a metastable ("monotropic") liquid crystal II, which may at any moment revert to the stable solid-crystalline form. The ethyl compound melts directly to an isotropic liquid at 73°, but when this is cooled it passes into a liquid-crystal I at 61° and a liquid-crystal II at 45°, both being metastable and monotropic and reverting spontaneously to the solid form. Both substances behave as positive uniaxial crystals, with optic axes perpendicular to the plane of the film. The wave-lengths used were Li 6708, Na 5893, Hg 5461, Hg 4357—a series which presents substantial advantages over the conventional series H_α, Na, H_β, H_γ.[53] Observation by means of thin films gave the following values:

[49] *Ann. Physik*, 1900, [iv], **2**, 661.
[50] *Ibid.*, 1905, **18**, 796.
[51] *Ber.*, 1908, **31**, 2033; *A.*, 1908, i, 641.
[52] E. Dorn and W. Lohmann, *Ann. Physik*, 1909, [iv], **29**, 533; *A.*, 1909, ii, 529.
[53] Compare *Phil. Mag.*, 1909, [vi], **18**, 320; *A.*, 1909, ii, 774.

Ethyl Compound.

		Isotropic.		Liquid-crystal I (ord. ray).		Liquid-crystal II (ord. ray).[54]	
		100°.	60°.	45°.	30°.	30°.	27°.
Li.........	6708	1·5943	1·6134	1·5453	1·5371	1·5249	1·5211
Na	5893	1·6118	1·6308	1·5523	1·5408	1·5332	1·5286
Hg	5461	1·6239	1·6440	1·5625	1·5504	1·5400	1·5337
Hg	4357	1·6742	1·6955	1·6166	1·5956	1·5794	1·5687

Methyl Compound.

		Isotropic.		Liquid-crystal I (ord. ray).		Liquid-crystal II (ord. ray).[54]	
		145°.	125°.	100°.	80°.	70°.	40°.
Li.........	6708	1·5860	1·5945	1·5227	1·5150	1·5062	1·5082
Na	5893	1·6021	1·6097	1·5359	1·5283	1·5160	1·5170
Hg	5461	1·6148	1·6242	1·5424	1·5341	1·5198	1·5208
Hg	4357	[Refraction too high for measurement]				1·5522	1·5501

The refractive indices for the extraordinary ray (and some of the ordinary refractive indices for λ 4357) were too high to be measured by total reflection. Observations by means of Newton's rings gave the values:

		Ethyl Compound. Liquid-crystal II, 28°		*Methyl Compound.* Liquid-crystal II.	
		Ord.	Ex.	Ord.	Ex.
Li	6708	1·522	1·885	1·511	1·869
Na	5893	1·529	1·907	1·518	1·910
Hg	5461	1·535	1·936	1·522	1·921
Hg	4357	1·570	2·207	1·551	2·170

These figures are very remarkable, as they indicate a double refraction, which for blue light is *more than three times as great as in the case of calcite.*

Typical values for the double refraction of the liquid-crystal I forms[55] are as follows:

	Ethyl Compound.		*Methyl Compound.*	
Na 5893.	59°.	45°.	116°.	86°.
Ord................	1·571	1·552	1·546	1·529
Ex.	1·751	1·809	1·756	1·833

It should be noticed that the double refraction decreases with rising temperature, the ordinary coefficient increasing and the

[54] The exceptionally large temperature-coefficient for the ethyl compound is in marked contrast with the small (±) coefficient for the methyl compound.

[55] E. Dorn, *Physikal. Zeitsch.*, 1910, **11**, 777 ; *A.*, ii, 809.

extraordinary coefficient decreasing in such a way as to converge towards the intermediate values for the isotropic liquid.

In the case of cholesteryl propionate,[56] the double refraction of which is positive, the refractive indices for the isotropic liquid and for *both* rays in the crystalline liquid decrease with rising temperature, but here again the values for the two rays converge towards those for the isotropic liquid. Measurements made at the same temperature give for the isotropic liquid values agreeing almost exactly with the mean of the two values for the anisotropic liquid; thus, for Na 5893, the values found were as follows:

	82°.	100°.	110°.	129°.
Ord. ray	1·500	1·492	1·487	—
Ex. ray	1·478	1·474	1·472	—
Mean	1·489	1·483	1·4795	—
Isotropic	—	1·482	1·480	1·475

Another property characteristic of some solid uniaxial crystals, namely, that of rotating the plane of polarised light travelling along the optic axis, has also been detected recently in the case of liquid crystals of certain active amyl esters,[57] namely, amyl *p*-methoxybenzylideneamino-cinnamate and -*α*-methylcinnamate and amyl *p*-ethoxybenzylideneamino-*α*-ethylcinnamate. These transparent substances have the property of producing in the case of polarised light travelling along the optic axis a rotation of extraordinary magnitude; for instance, a layer composed of equal parts of the two *p*-methoxybenzylidene compounds and only 0·02 mm. thick produced a rotation of 106°, or 5300° per mm., as contrasted with 21° per mm. for quartz.[58] A fuller investigation of this phenomenon has been carried out by F. Stumpf [59] in the case of active amyl *p*-cyanobenzylideneaminocinnamate.[60] The solid crystals of this substance pass at 92° into a second solid, and a first liquid, crystalline modification, which in turn gives place to a second liquid-crystalline modification at 98°, and becomes an isotropic liquid at 105°; the experiments were carried out with the first liquid-crystalline phase, which can be supercooled to 75°. As in the case of the three substances examined by Dorn and Lohmann, the double refraction was found to decrease with rising temperature, the ordinary index of refraction decreasing and the extraordinary index increasing in such a way as to converge towards the intermediate value for the isotropic liquid.

In order to avoid errors arising from the measurement of a very

[56] E. Dorn, *loc. cit.*

[57] D. Vorländer, *Ber.*, 1908, **41**, 2033; *A.*, 1908, i, 641.

[58] The values for quartz exceed those for the majority of optically active liquids in the ratio of 10—100 : 1.

[59] *Physikal. Zeitsch.*, 1910, **11**, 780; *A.*, ii, 809.

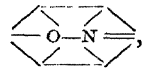
[60] O. Lehmann and M. E. Huth, *Diss.*, Halle, 1909.

thin film, the ester was examined between a lens and a flat plate, both alone and mixed with half its weight of *p*-cyanobenzylideneanisidine. The mixture showed anomalous rotatory dispersion, falling from 36,000° per mm. at 20° in the violet to 15,000° in the yellowish-green, and rising again to 19,000° in the red; the anomalous rotatory dispersion is closely related to the absorptive properties of the liquid—for very deep red light, the transmitted ray shows complete circular polarisation, the other circularly polarised constituent being completely absorbed. In the pure ester, the maximum absorption falls well within the limits of the visible spectrum, in the yellow, the sign of the rotation being different on either side of the band; a minimum rotation is again recorded on the violet side of the band.

The brilliant iridescence of some liquid crystals has been shown to be associated with the selective absorption, transmission, or reflection of circularly polarised light by optically active liquid crystals.[61]

Several attempts have been made to associate the production of liquid crystals with particular types of molecular structure, for instance, $XO\cdot C_6H_4\cdot N_2O\cdot C_6H_4\cdot OX$ and $XO\cdot C_6H_4\cdot CH\colon CH\cdot CO_2X$. T. Rotarski[62] has called attention to the formation of liquid crystals of the compounds:

$(\cdot CH\colon CH\cdot C_6H_4\cdot O\cdot CH_3)_2$, $C_6H_5\cdot NH\cdot N\colon CH\cdot C_6H_4\cdot NH\cdot CH_3$,
and $C_2H_5\cdot NH\cdot C_6H_4\cdot C_6H_4\cdot NH\cdot C_2H_5$,

all of which contain a benzene ring linked to OX or NHX on one side, and $-CH\colon CH\cdot CH\colon N-$ or $-C_6H_4X$ on the other side. He has also put forward a theory[63] which represents the liquid crystal as an intermediate phase between an open molecular system in the isotropic liquid and a closed molecular system in the crystalline solid. The analogy is suggested of nitrosobenzene, which gives colourless crystals formulated as , and a green liquid formulated as —N=O, although in this case the intermediate liquid-crystal form is not developed. Vorländer[64] has studied the effect of substitution on the formation of liquid crystals of the cinnamic series. Theories as to the nature of liquid crystals have also been put forward by P. N. Pawloff[65] and by G. Wulff[66];

61 F. Stumpf, *loc. cit.*; F. Giesel, *Physikal. Zeitsch.*, 1910, **11**, 192; *A.*, ii, 371.

62 *Ber.*, 1908, **41**, 1994; *A.*, 1908, i, 640.

63 *J. pr. Chem.*, 1910, [ii], **82**, 23; *A.* ii, 685.

64 *Ber.*, 1908, **41**, 2033; *A.*, 1908, i, 641.

65 *J. Russ. Phys. Chem. Soc.*, 1909, **41**, 685; *A.*, 1909, ii, 800. Compare P. P. von Weimarn, *Zeitsch. Chem. Ind. Kolloide*, 1909, **4**, 59; *A.*, ii, 301.

66 *Zeitsch. Kryst. Min.*, 1909, **46**, 261; *A.*, ii, 473.

but these do not present any marked advantage over the original theory of Lehmann, that liquid crystals are merely crystals in which the elastic limit or rigidity has been reduced to zero.

Specific Heats of Elements and Compounds.

A number of new values have recently been given for the specific and atomic heats of elements, especially at low temperatures. A. Magnus,[67] using two similar calorimeters, each containing 60 litres of water, measured the difference of temperature between them by means of a copper-constantan thermopile of 100 elements, and obtained a deflection of 0·1 mm. for a change of temperature of 0·00002°. The following values obtained by this method are probably subject to error in the fourth significant figure only.

		Sp. ht.	At. ht.			Mol. ht.
Pb	18—100°	0·03095	6·409	$PbCl_2$	15—100°	18·52
	16—256	0·03189	6·606		16—350	19·58
Al	16—100	0·2122	5·750	AgCl	15—100	13·01
	17—547	0·2389	6·475		16—300	13·72
Ag	17—507	0·05985	6·460	PbI_2	17—100	19·70
	16—614	0·06154	6·641		18—250	20·75
Cu	15—238	0·09510	6·048	HgCl	15—100	12·48
	15—338	0·09575	6·090	AgI	19—100	13 82

W. Nernst, F. Koref, and F. A. Lindemann[68] have introduced a novel type of calorimeter, consisting of a cylindrical block of copper, enclosed for the purpose of heat-insulation in a vacuum vessel, the heat capacity of the substance to be tested being deduced from the rise of temperature of the copper block instead of from the rise of temperature of a fluid. The chief merit of the calorimeter is that it can be used over a very wide range of temperatures. The following values, amongst others, were determined:

Substance.	Temperature.	Sp. ht.	At. ht.
Cu	21·6 to 2·4°	0·09155	5·82
Zn	20·2 to 1·74	0·0949	6·206
	−76·3 to −2·0	0·0906	5·922
Pb	−76·8 to −3·0	0·03003	6·22
Al	−76·0 to 1·2	0·1962	5·32
S (rh.)	30·6 to 1·0	0·1708	5·48
	0·0 to −76·9	0·1537	4·93
	−189·5 to −80·7	0·1131	3·63
S (mon.)	43·4 to 1·9	0·1794	5·75
	0·0 to −76·2	0·1612	5·17
	−189·0 to −80·1	0·1187	3·80
I	47·0 to 1·8	0·0524	6·64
	−76·4 to −0·5	0·0516	6·364
	−189·0 to −6·1	0·04669	5·92

[67] *Ann. Physik*, 1910, [iv], **31**, 597; *A.*, ii, 262.

[68] *Sitzungsber. K. Akad. Wiss. Berlin*, 1910, 247; *A.*, ii, 263. Compare Dewar, *Proc. Roy. Soc.*, 1905, A, **76**, 330; *A.*, 1905, ii, 801.

Substance.	Temperature.	Sp. ht.	Mol. ht.	Diff.
Ice	−76·9 to −2·9	0·4329	7·80	
	−15·3 to −75·9	0·4170	7·515	
	−189·5 to −81·7	0·2658	4·79	
$H_2C_2O_4+2H_2O$	46·6 to 3·24	0·3742	47·13	2 × 11·5
$H_2C_2O_4$	47·0 to 1·84	0·2785	24·06	
$H_2C_2O_4+2H_2O$	0·0 to −75·2	0·2969	37·39	2 × 8·50
$H_2C_2O_4$	0·0 to −75·8	0·2263	20·39	
$H_2C_2O_4+2H_2O$	−190·6 to −81·9	0·1975	24·91	2 × 5·35
$H_2C_2O_4$	−189·0 to −81·9	0·1580	14·22	
$K_4FeC_6N_6+3H_2O$	0·0 to −76·5	0·2533	107·1	3 × 12·0
$K_4FeC_6N_6$	0·0 to −77·0	0·1932	71·2	
$K_4FeC_6N_6+3H_2O$	−188·7 to −8·1	0·2046	86·5	
$K_4FeC_6N_6$	−190·8 to −80·7	0·1400	51·5	
$Na_2HPO_4+12H_2O$ ...	0·0 to −75·3	0·3527	126·4	5 × 5·7
$Na_2HPO_4+7H_2O$ ...	0·0 to −75·3	0·3095	83·1	
$CuSO_4+H_2O$	0·0 to −77·5	0·1535	27·28	6·50
$CuSO_4$	0·0 to −77·1	0·1302	20·78	
$CuSO_4+H_2O$	−189·0 to −79·7	0·1026	18·24	4·16
$CuSO_4$	−188·7 to −80·2	0·0882	14·08	

An independent determination of the average specific heat of rhombic sulphur between 23° and 92° [69] has given the values: specific heat, 0·176; atomic heat, 5·63.

In another novel type of calorimeter described by W. Nernst,[70] the substance under investigation is used as the calorimetric medium. A known quantity of heat is supplied to the substance by means of a thin platinum wire embedded in it, and the rise of temperature is deduced from the measured increase in the electrical resistance of the wire. The thermal isolation of the substance is effected by suspending it in an exhausted vessel, the effectiveness of the evacuation being checked by means of an attached Geissler tube. The chief merit of this type of apparatus is that it can be used to measure the specific heat over a very narrow interval of temperature and at any point on the thermometric scale. The following values for a series of exact temperatures were calculated by means of interpolation formulæ from the experimental measurements:

	Molecular Heat of							
	0°.	−30°.	−60°.	−90°.	−120°.	−150°.	−180°.	−210°
Lead	6·31	6·25	6·17	6·09	5·99	5·89	5·77	5·65
Silver	6·00	5·92	5·83	5·70	5·52	5·29	4·71	3·70
Ice	—	8·11	7·06	6·14	5·28	4·42	3·58	—

Values are also given for a series of anhydrous and hydrated salts. Attention is directed to the rapid decrease of specific heat which takes place at low temperatures. In the case of lead, the atomic heat from +69° to −40° is expressed by the formula $6·31+0·002t$; but from −80° to −210° an additional negative term must be introduced, as shown by the formula $6·31+0·002t-0·0000055t^2$.

[69] W. A. Kurbatoff, *J. Russ. Phys. Chem Soc.*, 1909, **41**, 311; *A.*, 1909, ii, 465.
[70] *Sitzungsber. K. Akad. Wiss. Berlin*, 1910, 262; *A.*, ii, 263.

In the case of silver the decrease of specific heat is more rapid, whilst the value for the molecular heat of ice, which falls to 3·30 at −190°, has been shown by Dewar[71] to be only 2·63 over the range from −188° to −252·5°. It is suggested that the observations now recorded are compatible with Einstein's theory, according to which the specific heats of crystalline and amorphous solids should vanish at the absolute zero.

Experiments on the "Specific Heat of the Elements at Low Temperatures" have also been made by T. W. Richards and F. G. Jackson,[72] who give an admirable summary of the earlier work of Person (1847), Regnault (1849), Pebal and Jahn (1889), Behn (1897–1900), Trowbridge (1898), Tilden (1900), and Schmitz (1903). Special tests were made to determine the gain of heat by the cold object during the period of transference from the liquid-air bath to the water of the calorimeter, and the cooling due to cold air transferred with the object; the latter factor was the more important, as identical values (a cooling of 0·0065° and 0·007°) were found for the correction when determined by pouring an empty receptacle into the calorimeter, and by comparing the fall of temperature produced by a solid and a hollow copper cylinder of similar shape, but of widely different weights. The following values were deduced for the atomic heats of the chief elements:

Element.	At. wt.	Sp. ht. −188 to +20°.	At. ht. −188 to +20°.	At. ht. +20 to +100°.	Diff.
C	12·00	0·0959	1·15	2·4	1·2
Mg......	24·32	0·208	5·06	6·0	1·0
Al	27·1	0·1748	4·73	5·8	1·1
Si	28·3	0·118	3·34	5·2	1·9
P	31·0	0·169	5·24	6·3	1·1
S.........	32·07	0·131	4·20	5·6	1·4
Cr	52·1	0·0794	4·14	5·6	1·5
Mn......	54·93	0·0931	5·12	6·7	1·6
Fe	55·85	0·0859	4·78	6·5	1·7
Ni	58·68	0·0869	5·09	6 3	1·2
Co	58·97	0·0828	4·88	6·2	1·3
Cu	63·57	0·0789	5·01	5·9	0·9
Zn	65·37	0·0846	5·53	6·1	0·6
As	75·0	0·0705	5·29	6·2	0·9
Mo......	96 0	0·0555	5·33	5·7	0·4
Pd	106·7	0·0517	5·51	6·3	0·8
Ag	107·88	0·0511	5·51	6·1	0·6
Cd	112·4	0·0515	5·79	6·2	0·4
Sn	119·0	0·0502	5·97	6·5	0·5
Sb	120·1	0·0469	5·62	6·0	0·4
Pt	195·0	0·0279	5·45	6·3	0·8
Au.. ...	197·2	0·0297	5·86	6·1	0·2
Tl	204·0	0·0296	6·04	6·7	0·7
Pb	207·1	0·0300	6·21	6·3	0·1
Bi	208·0	0·0284	5 91	6·3	0·4
Average	—	—	5·06	5·98	0·92

[71] *Proc. Roy. Soc.*, 1905, A, **76**, 330; *A.*, 1905, ii, 801.
[72] *Zeitsch. physikal. Chem.*, 1910, **70**, 414; *A.*, ii, 264.

The increase of atomic heat with rise of temperature is seen to become less as the atomic weight increases, and if the members of any given family of elements are picked out, the lessening is seen to take place in a very regular way.

The significance of Richards' observations has been discussed by A. Magnus and F. A. Lindemann [73] from the point of view of Einstein's development of Planck's radiation-theory.[74]

H. Schimpff,[75] who has carried out an investigation on similar lines, gives (in addition to the values over the ranges 17° to 100°, 17° to −75°, and 17° to −190°) the following table of values of the atomic heats of the metals at a series of fixed temperatures:

	−150°.	−100°.	−50°.	0°.	50°.
Mg	4·30	4·93	5·43	5·79	6·02
Al	3·71	4·54	5·19	5·63	5·89
Si	2·31	3·21	3·95	4·54	4·96
Cr	3·12	4·13	4·90	5·44	5·74
Ni	3·86	4·79	5·52	6·06	6·39
Co	3·97	4·77	5·39	5·83	6 08
Sb	4 95	5·39	5·72	5·94	6·05
Au	5·25	5·54	5·78	5·97	6·10
Pb	5·77	5·85	5·97	6·14	6·37
Bi	5·49	5·67	5 86	6·06	6·27
Cu	4·29	4·98	5·48	5·79	5·90
Zn	4·84	5·32	5·70	5·96	6·11
Ag	4·97	5·46	5·80	6·01	6·06
Sn	5·36	5·75	6·09	6·38	6·59

The atomic heats are seen to diverge in a marked way as the temperature falls, whilst conversely a rise of temperature produces, as is well known, a marked convergence towards a fixed value for all the elements. In the case of a series of metallic compounds, the specific heat usually agreed within the limits of experimental error (estimated at 2 per cent.) with the value calculated for a mixture of the constituents, and only in very rare cases did the difference exceed 4 per cent.

Specific Heats of Gases.

Measurements of the specific heats of gases have been made both at ordinary and at high temperatures. W. F. G. Swann [76] has determined the specific heat of air and of carbon dioxide by a continuous electrical method, in which the gas was supplied with definite quantities of energy by passing over a heated platinum coil of 1 ohm resistance, separating two 12 ohm platinum

[73] *Zeitsch. Elektrochem.*, 1910, **16**, 269 ; *A.*, ii, 580.
[74] *Ann. Physik*, 1907, [iv], **22**, 180.
[75] *Zeitsch. physikal. Chem.*, 1910, **71**, 257 ; *A.*, ii, 181.
[76] *Proc. Roy. Soc.*, 1909, **82**, A, 147 ; *A.*, 1909, ii. 465.

resistances which were used differentially to determine the rise of temperature. The values found:

Air	0·24173 cal.	per gram-degree	at	20°
	0·24301	,,	,,	100
Carbon dioxide	0·20202	,,	,,	20
	0·22120	,,	,,	100

are probably correct within about 1 part in 1000, but exceed the earlier values by about 2 per cent., probably owing to underestimation of the correction for flow of heat between the heater and calorimeter in the experiments of Regnault and others.

A continuous-flow method has also been applied by W. Nernst [77] in the case of ammonia gas at higher temperatures. The gas was heated to a measured temperature by passing it through a copper cylinder packed with silver foil, and partly enclosed in an electric furnace heated to constant temperature. From the heater the gas passed to a silver block, enclosed in the electric furnace, traversing the block eight times before escaping into the air. When no gas was passing, the block acquired accurately the temperature of the walls of the furnace, but on passing the gas it became cooled to an extent depending on the specific heat of the gas, the rate of flow, and the steady difference of temperature (about 200°) between the heater and the silver block. The apparatus was calibrated by means of carbon dioxide (using the values given by Holborn and Henning),[78] oxygen, and steam (using the values given by Pier).[79] The values obtained for the molecular heat at constant pressure were found to agree (like those at lower temperatures) with values calculated from the formula:

$$C_p = 8{\cdot}62 + 0{\cdot}0020t + 7{\cdot}2 \times 10^{-9}t^3,$$

as is shown by the following comparison, in which the values below 300° are by Keutel, Voller, Wiedemann, and Regnault:

	20°.	25—100°.	25—200°.	24—216°.	365—567°.	480—680°.
C_p (obs.)	8·65	8·84	9·11	8·71	10·4	11·2
C_p (calc.)	8·66	8·74	8·86	8·88	10·3	11·2

From these figures the heat of formation of ammonia gas at 850° is calculated to be 30,220 cal., a figure somewhat higher than the values that have been found experimentally.

The methods of determining the specific heat of a gas at constant volume in the higher ranges of temperature by measuring the maximum pressure (and thence deducing the maximum temperature) reached in a gaseous explosion were introduced many years ago by Berthelot and Vieille and by Le Chatelier. The chief disadvantages

77 *Zeitsch. Elektrochem.*, 1910, **16**, 96; *A.*, ii, 265.
78 *Ann. Physik*, 1907, [iv], **23**, 809; *A.*, 1907, ii, 844.
79 *Vide infra.*

of the method were that no independent values were available for comparison, and that the mass of the moving parts of the pressure-gauge caused a lag in the recording of the maximum pressure, and an oscillatory motion during the subsequent decay of pressure caused by the cooling of the products. The first difficulty has been overcome by the work of Holborn and Henning,[80] which resulted in the case of nitrogen in a close agreement between their direct measurements at temperatures up to 1400° and the values previously deduced from explosion experiments; the lower values which they obtained for steam and for carbon dioxide were no doubt due to the fact that in the explosion experiments heat was absorbed by the dissociation of these gases. The experimental difficulty of recording accurately the maximum pressure of explosion has been overcome by M. Pier,[81] who exploded electrolytic gas with various diluents in a steel bomb of 35 litres capacity (to reduce the cooling effect) and obtained absolutely sharp curves when recording the pressure by means of the deflection of a corrugated steel diaphragm, weighing less than a gram, and provided with a mirror to reflect a spot of light on to a rapidly moving photographic film. The accuracy of the method was established by the fact that argon, a monatomic gas—which under normal conditions gives the theoretical value 2·977 for its molecular heat at constant volume—gave the same value at temperatures of explosion ranging from 1435° to 2347°. Nitrogen and hydrogen gave values agreeing with the formulæ:

$$N_2 \quad C_v = 4{\cdot}900 + 0{\cdot}00045t$$
$$H_2 \quad C_v = 4{\cdot}700 + 0{\cdot}00045t$$

for the average molecular heat between 0° and t°. For water vapour between 0° and 2350°, the formula given is:

$$H_2O \quad C_v = 6{\cdot}065 + 0{\cdot}0005t + 0{\cdot}2 \times 10^{-9}t^3.$$

Hydrogen chloride agrees fairly well with the formula:

$$HCl \quad C_v = 4{\cdot}600 + 0{\cdot}0005t$$ [82]

In a later series of experiments,[83] acetylene was exploded with air, oxygen, and carbon dioxide, giving the molecular heats of oxygen and carbon dioxide in terms of that of nitrogen. The molecular heat of oxygen agrees, up to 2200°, with that of nitrogen; the values for carbon dioxide can be represented by the equation:

$$CO_2: C_v = 6{\cdot}800 + 3{\cdot}3 \times 10^{-3}t - 0{\cdot}95 \times 10^{-6}t^2 + 0{\cdot}1 \times 10^{-9}t^3;$$

sulphur dioxide agrees with carbon dioxide up to 2000°, the values being deduced from the results obtained by exploding carbon disulphide with oxygen.

80 *Loc. cit.*
81 *Zeitsch. Elektrochem.*, 1909, **15**, 536; *A.*, 1909, ii, 789.
82 M. Pier, *Zeitsch. physikal. Chem.*, 1909, **66**, 759; *A.*, 1909, ii, 542.
83 *Zeitsch. Elektrochem.*, 1910, **16**, 897; *A.*, ii, 1031.

Refractive Indices of Gases.

Whilst the refractive indices of liquids and solids present many complex features, especially in the case of unsaturated compounds, the study of the refractivity of gases has led to the recognition of relationships of remarkable simplicity. The measurements of Ramsay [84] suggested that the ratios of the refractivities of the inactive gases formed a simple integral series. The re-determination of the values for helium and argon by W. Burton,[85] for neon, xenon, and krypton by C. and M. Cuthbertson,[86] together with the dispersion values of all these gases,[87] confirmed the belief that the refractivities for infinite wave-lengths are in the ratio 1 : 2 : 8 : 12 : 20, the deviations amounting to −4, 0·3, 0·4, and −1·9 per cent. respectively for the four heavier gases, whilst a comparison for λ 5893 showed deviations of −1·9, 1·3, 1·6, and 0·3 per cent. The halogens and the members of the oxygen family form two similar series, in which the ratios are 2 : 8 : 12 : 20, whilst nitrogen, phosphorus, and arsenic give the ratio 2 : 8 : 12.[88] These simple ratios are probably related in an intimate way to the structures of the atoms in each family of elements. In the case of hydrogen, oxygen, and nitrogen, it has been shown [89] that the numerator N in the Sellmeier dispersion-formula $\mu - 1 = N/(n_0^2 - n^2)$ (where n_0 = frequency of free-period of the substance, and n = frequency of incident light) has the values 1·692, 3·397, and 5·0345 × 10^{27}, which are in the ratio 1 : 2 : 3 of the valencies of the three elements,[89a] with a maximum deviation of about 1 per cent.; on Drude's theory, the numerator N is proportional to the number of electrons in unit volume of the medium, a quantity which must evidently be related in a very close way to the chemical property of valency.

The refractive indices of the inactive gases are probably related to their viscosities, which have been determined by A. O. Rankine [90] by means of a novel apparatus, in which a pellet of mercury falling in a vertical tube is used to drive gas through a vertical capillary

[84] *Arch. Néerland.*, 1900, [ii], **5**, 356 ; *A.*, 1901, ii, 141. Compare Ramsay and Travers, *Proc. Roy. Soc.*, 1901, **67**, 329 ; *A.*, 1901, ii, 237.

[85] *Proc. Roy. Soc.*, 1908, A, **80**, 390 ; *A.*, 1908, ii, 345. Compare K. Scheel and R. Schmidt, *Ber. Deut. physikal. Ges.*, 1908, **6**, 207 ; *A.*, 1908, ii, 333, for helium.

[86] *Proc. Roy. Soc.*, 1908, A, **81**, 440 ; 1910, A, **83**, 149 ; *A*, 1909, ii, 105 ; *A.*, 1910, ii, 85.

[87] C. and M. Cuthbertson, *ibid.*, 1910, A, **84**, 13 ; *A.*, ii, 561.

[88] Cuthbertson and Metcalfe, *ibid.*, 1908, A, **80**, 411 ; *A.*, 1908, ii, 545.

[89] C. and M. Cuthbertson, *ibid.*, 1909, **83**, 151 ; *A.*, ii, 85.

[89a] The numerator for phosphorus corresponded with that for valency 3, but arsenic gave a fractional ratio 4·5.

[90] *Proc. Roy. Soc.*, 1910, A, **83**, 265, 516 ; **84**, 181 ; *A.*, ii, 188, 409, 429. Compare Schmitt, *Ann. Physik*, 1909, [iv], **30**, 393 ; *A.*, 1909, ii, 867.

tube, the two tubes being connected together both above and below. The viscosities relative to air were:

He.	Ne.	Ar.	Kr.	K.
1·086	1·721	1·221	1·361	1·234

whence the following relative values were deduced for the molecular constants of the five gases:

Gas.	Relative atomic weight.	Viscosity.	Mean free path.	Molecular radius.	Molecular volume.	Atomic density
He	1·00	1·000	1·000	1·00	1·00	1·00
Ne	5·06	1·585	0·704	1·19	1·69	2·99
A	10·08	1·124	0·354	1·68	4·74	2·12
Kr	20·96	1·253	0·274	1·91	6·98	3·00
X	33·01	1·136	0·198	2·25	11·37	2·90

It has since been shown [91] that linear relationships are observed when the constant N of the dispersion formula $\mu - 1 = N/(n_0^2 - n^2)$ is plotted against the square roots of the relative mean free paths of the molecules in the five gases at 0° and again at 100°. A linear relationship is also observed when N^2 is plotted against the critical temperatures of the gases, or against the radii of the spheres of action of their molecules.

G. Rudorf [92] has recorded certain numerical constants of radium emanation and their relation to those of the inert gases. Their solubility in water,[93] compressibility (of helium and neon),[94] and conductivity for heat (of helium, argon, and neon, with nine of the commoner gases) [95] have also been measured during the past year.

Electrical Properties of Pure Solvents.

In a series of recent papers [96] G. Jaffé has shown that liquid hexane, when carefully purified, exhibits most of the properties of a dense gas. The conductivity in a brass cylinder of 3·8 cm. internal diameter was about 12·6 times that of air, and was independent of the temperature, but depended on the material of the containing vessel; about two-thirds of the conductivity was shown to be due to ionisation caused by radiation from external radioactive substances. When the potential gradient exceeded 200 volts/cm., the current was independent of the voltage, as in the case of the "saturation-current" of a gas. The specific velocities of the positive and negative ions produced in the liquid by means

[91] C. Cuthbertson, *Phil. Mag.*, 1911, [vi], **21**, 69.

[92] *Zeitsch. Elektrochem.*, 1909, **15**, 748; *A.*, 1909, ii, 954.

[93] A. von Antropoff, *Proc. Roy. Soc.*, 1910, A, **83**, 474; *A.*, ii, 409.

[94] F. P. Burt, *Trans. Faraday Soc.*, 1910, **6**, 19; *A.*, ii, 823.

[95] F. Soddy and A. J. Berry, *Proc. Roy. Soc.*, 1910, A, **83**, 254; *A.*, ii, 180.

[96] *Ann. Physik*, 1909, [iv], **28**, 326; 1910, [iv], **32**, 148; *Physikal. Zeitsch.*, 1910, **11**, 571; *A.*, 1909, ii, 462; 1910, ii, 481, 681.

of radium were measured, and their rate of recombination was determined by the same methods as in the case of gases; zinc immersed in hexane and exposed to ultra-violet light gave rise to photoelectric effects analogous to those observed in air.

The most effective method of purification in the case of hexane was to subject the liquid for a long period to the action of a large electromotive force. This method has been applied by J. Schröder[97] in the case of ethyl ether, which differs from hexane in having the properties of a weak ionising solvent; by heating the platinum electrodes to redness to remove volatile impurities, and purifying by the method just indicated, the discrepancies which were noticed at first were got rid of as in the case of hexane, and the existence of a saturation current was again indicated.

A most important advance has been effected by the application of the same method to liquid sulphur dioxide,[98] whereby the specific resistance at low voltages was raised to $7 \cdot 6 \times 10^9$—a figure 700 times greater than that recorded by Walden and Centnerszwer[99]—and at 2350 to 4000 volts to 5×10^{10}. At 5000 volts the sulphur dioxide appears to be decomposed by the current. In view of the fact that sulphur dioxide gives electrolytic solutions the conductivity of which is but little inferior to that of aqueous solutions, it is of great interest to know that the pure solvent does not obey Ohm's law, but approximates rather to the electrical behaviour of a gas. The suggestion that all ionising solvents have a minimum specific conductivity approximating to Kohlrausch's value for purified water (0·04 gemmhos) must evidently be abandoned, and the problem of still further reducing the conductivity of water itself may now be attacked with a greatly increased prospect of success.

During the same period new determinations have been made of the ionisation constant of water as it exists in various aqueous solutions. A. Heydweiller[1] has given for the ionisation constant the values:

Temperature ...	0°	10°	18°	25°	50°	100°	150°	200
$K_w \times 10^{14}$	0·116	0·281	0·59	1·04	5·66	58·2	234	525

where $K_w = a^2/1 - a$ and a = the quantity of ionised water in a litre. These values are about 25 per cent. larger than those given by A. A. Noyes, Y. Kato, and R. B. Sosman,[2] whose figures for the hydrogen-ion concentration are:

Temperature	0°	18°	25°	100°	156°	218°	306°
Concentration	0·30	0·68	0·91	6·9	14·9	21·5	$18 \cdot 0 \times 10^{-7}$

[97] *Ann. Physik*, 1909, [iv], **29**, 125; *A.*, 1909, ii, 462.
[98] J. Carvallo, *Compt. rend.*, 1910, **151**, 717; *A.*, ii, 1026.
[99] *Zeitsch. physikal. Chem.*, 1901, **39**, 514; *A.*, 1902, ii, 245.
[1] *Ann. Physik*, 1909, [iv], **28**, 503; *A.*, 1909, ii, 292.
[2] *J. Amer. Chem. Soc.*, 1910, **32**, 159; *A.*, ii, 257.

For the degree of dissociation of water at different temperatures, R. Lorenz and A. Böhi [3] have given the values:

Temperature	0°	18°	25°	40°	60°	80°	90°
Degree of dissociation	0·37	0·85	1·10	1·98	3·55	5·92	$7{\cdot}30 \times 10^{-7}$

Compare also C. S. Hudson [4] for a method based on the mutarotation of the sugars.

Transference Numbers.

Hittorf's method of determining transference numbers from the changes of concentration which take place at the electrodes during electrolysis is known to give results which differ somewhat from those deduced by actual measurements of velocity in Lodge's "moving-boundary" method. The difference has been attributed to the transport of water during electrolysis, and "true transference numbers" have been deduced from the motion of the electrolyte relatively to some non-electrolyte, such as mannitol, resorcinol, sucrose, raffinose, or arsenious acid added to the solution.[5] Typical values obtained by the three methods are:

	Hittorf-method.	"True."	Boundary-method.
KCl (normal)	0·515	0·505	0·508
NaCl (normal).........	0·631	0·613	0·614

On account of the close agreement between them it has been assumed [6] that the boundary method gives directly the "true" transference numbers. It has, however, been pointed out by G. N. Lewis [7] that the boundaries are subject to displacement owing to changes of volume taking place at the electrodes; it is suggested that these should be measured, and that the electrolysis should be carried out in a tube open at one end only, in order that the displacement may take place in a definite way; when a correction for displacement is applied, the method of moving boundaries gives, both in theory and in practice, transference numbers identical with those obtained by Hittorf's method.

Determinations of transport numbers have been carried out in the laboratory of A. A. Noyes by a method which depends on measuring the electromotive force set up in a solution by centrifugal action,[8] a method introduced by Des Coudres in 1893 in order to intensify the weak gravitational effects noticed by Colley

[3] *Zeitsch. physikal. Chem.*, 1909, **66**, 733; *A.*, 1909, ii, 541.

[4] *J. Amer. Chem. Soc.*, 1909, **31**, 1136; *A.*, 1909, ii, 855.

[5] G. Buckböck, *Zeitsch. physikal. Chem.*, 1906, **55**, 563; *A.*, 1906, ii, 519; E. W. Washburn, *Tech. Quart.*, 1908, **21**, 288; *A.*, 1908, ii, 1009.

[6] Washburn, *loc. cit.* Denison, *Trans. Faraday Soc.*, 1909, **5**, 165; *A.*, ii, 15.

[7] *J. Amer. Chem. Soc.*, 1910, **32**, 862; *A.*, ii, 683.

[8] R. C. Tolman, *Proc. Amer. Acad.*, 1910, **46**, 109.

(1875–1882). The centrifuge, of special design, was driven by a steam turbine of 30 h.p. at speeds up to 7850 r.p.m., but the glass tubes containing the solutions could only be used at much lower speeds producing electromotive forces up to 6 millivolts. The transport numbers deduced from the centrifugal experiments for a series of iodides are in good agreement with those obtained by other methods.

Determinations of the transport number of hydrochloric acid by Hittorf's method have been made at moderate dilutions by E. H. Riesenfeld and B. Reinhold,[9] who gave the values:

for 0·977 *N*	0·452 *N*	0·104 *N*
n = 0·155	0·155	0·161

and by C. Chittock,[10] who has detected a marked increase at extreme dilutions, probably owing to the retardation of the cation by the neutralisation of acid by ammonia, thus:

for 0·0014 *N*	0·0001 *N*
n = 0·171	0·275

Conductivity and Ionisation.

The curious curves of molecular conductivity observed by Franklin and others in the case of various solutions in ammonia and the amines[11] have now been detected in the case of concentrated aqueous solutions at 0°.[12] The figures given for potassium iodide:

v =	0·1766	0·1845	0·2075	0·2371	0·2760	0·2767	0·3320	0·4150	0·5534	0·664
μ =	57·3	59·2	64·3	65·2	67·8	67·7	69·3	70·4	70·8	70·4
									Max. (?)	
v =	0·830	1·328	1·660	2·651	3·32	4·15	5·31	7·81	10·62	13·28	21·28
μ =	70·6	70·5	70·7	70·8	71·6	72·0	72·4	73·1	74·1	74·6	75·6
		Min. (?)									

show a very shallow maximum and minimum at intermediate dilutions. In the case of potassium bromide, no actual maximum or minimum was reached, but the curve was found to approximate towards the same type.

The following values for the ionisation of sulphuric acid are given by A. A. Noyes and M. A. Stewart,[13] and are of general interest:

		From conductivity.			From freezing point.		
		H_2SO_4.	$H + HSO_4$.	$2H + SO_4$.	H_2SO_4.	$H + HSO_4$.	$2H + SO_4$.
At 0°	*M*/20	6	50	44	6	66	28
	M/40	5	42	53	5	58	37
	M/200	2	29	69	2	37	61

[9] *Zeitsch. physikal. Chem.*, 1909, **68**, 440; *A.*, ii, 14.
[10] *Proc. Camb. Phil. Soc.*, 1909, **15**, 55; *A.*, 1909, ii, 293.
[11] *Ann. Report*, 1909, 29.
[12] W. H. Sloan, *J. Amer. Chem. Soc.*, 1910, **32**, 946; *A.*, ii, 820.
[13] *Ibid.*, 1133; *A.*, ii, 937.

		From conductivity.			From isohydric data.		
At 25°	$M/20$	6	63	31	6	71	23%
	$M/40$	5	57	38	5	65	30
	$M/200$	2	34	64	2	31	67

For the methods used in deducing these values, and for similar determinations in the case of sodium hydrogen sulphate, reference may be made to the original paper.

T. MARTIN LOWRY.

INORGANIC CHEMISTRY.

No great outstanding discoveries have been made in this branch of the subject during the year, but many facts of great practical and theoretical interest have been added to the literature. A tendency which becomes more and more marked year by year is the study of reactions in inorganic chemistry by physico-chemical methods. So much is this the case that the inorganic chemist pure and simple has almost ceased to exist. The tendency is all for good so long as the chemist does not mistake his means for the end. The introduction of the methods of physical chemistry into organic chemistry has also made great strides, and it may be that, in the near future, the distinction made in the abstracts published by this and other societies may become so artificial as to lead to its abolition.

Atomic Weights.

The International Committee decided to alter the time of the publication of their report on the year's work on atomic weights, so that students and others might have it in hand before the beginning of the academical year. It will not be necessary therefore for this report to deal with researches on this subject which were published in the earlier part of the year, unless they involve principles of general interest apart from the question of accuracy to the second place of decimals. One of the most important researches published is one which gives independent values for lithium, chlorine, and silver.[1] Great precautions to ensure the purity of material and accuracy of manipulation were taken, and by the use of the comparative insolubility of lithium fluoride, the lithium salts were prepared free from the salts of the other alkali metals. The ratio of lithium chloride to silver chloride was determined with two specimens of lithium chloride, prepared (1) by the decomposition of lithium perchlorate, and (2) by conversion of lithium nitrate into carbonate, and thence into the chloride, by means of hydrochloric acid. The mean of seven determinations of the ratio $AgCl:LiCl$ gave 6·940,

[1] T. W. Richards and H. H. Willard, *J. Amer. Chem. Soc.*, 1910, **32**, 4; *A.*, ii, 292.

and the mean of seven determinations of the ratio Ag : LiCl gave 6·939 for the atomic weight of lithium (Ag = 107·880). The ratio of lithium chloride to lithium perchlorate was determined directly, the weighed lithium chloride being converted into the perchlorate by means of perchloric acid, and the perchlorate dried by fusion and weighed. Combining the ratio thus obtained, LiCl : 4O, with the ratio LiCl : Ag previously determined, the ratio Ag : 4O was calculated, and the atomic weight of silver deduced from this ratio was found to be 107·871, differing from the accepted value by 1 part in 12,000.

In the paper reference is again made to the unsatisfactory state of our knowledge with regard to the atomic weight of silver. The authors state that, since most other elements are referred to oxygen through silver, their atomic weights cannot be accurately known until the ratio between silver and oxygen is definitely established. It may be mentioned that experiments are in progress in the writer's laboratory the object of which is the direct determination of this ratio by the analysis of silver oxide. The difficulty of the drying of this substance seems, if one may judge from preliminary experiments, to have been effectively surmounted.

Strontium.—Sir Edward Thorpe and A. G. Francis [2] have determined six ratios in the investigation of the atomic weight of strontium. The mean of twenty-nine determinations gives 87·646 for the atomic weight.

Mercury.—Continuing his work of last year,[3] C. W. Easley has published a second paper,[4] which seems to confirm the abnormally high number of 200·62 for this constant. The ratio $HgCl_2$: Hg was studied, being determined (1) by a precipitation method, (2) by electrolysis. Previous determinations by other workers have not been altogether satisfactory, but an increase of more than 1 in 300 in the atomic weight will scarcely be accepted without confirmation, especially as the author admits that one of the methods used was open to doubt.

Tantalum.—The atomic weight of this element in the best previous determinations shows discrepancies amounting to nearly two units, and the new determination by C. W. Balke [5] was much needed. Tantalum chloride was prepared by heating the oxide in a mixture of chlorine and sulphur chloride vapour. By a process of fractional distillation, the sulphur chloride was separated from the tantalum chloride, the difference in boiling points being more than 100°. The tantalum chloride was shown to be free from sulphur. The

[2] *Proc. Roy. Soc.*, 1910, A, **83**, 277 ; *A.*, ii, 209.
[3] *J. Amer. Chem. Soc.*, 1909, **31**, 1207 ; *A.*, 1909, ii, 1013.
[4] *Ibid.*, 1910, **32**, 1117 ; *A.*, ii, 957.
[5] *Ibid.*, 1127 ; *A.*, ii, 962.

ratio $2TaCl_5 : Ta_2O_5$ was determined by allowing the chloride contained in a fused silica flask to hydrolyse slowly over water. After two or three days, liquid water and a little nitric acid were added, and carefully evaporated to dryness. It was finally ignited in a blast flame. Eight determinations, which show satisfactory concordance, give an atomic weight for tantalum of 181·52 (Cl = 35·46), a result which is 0·5 higher than the number last given by the International Committee. The work is being continued.

Tellurium.—From determinations of the loss in weight of telluric acid on heating, Marckwald [6] drew the conclusion that the atomic weight of tellurium was 126·85, which would bring the element into a normal position in the periodic classification. This result was criticised [7] on the ground that, so far as had been investigated, salts with water of crystallisation were untrustworthy as regards the constancy of their water content. Marckwald [8] has now redetermined the atomic weight of tellurium, using the dioxide obtained from telluric acid, which had been recrystallised several hundred times. This was converted into telluric acid by a volumetric process, and the mean atomic weight found was 127·61, thus confirming the work of former investigators. Marckwald now considers that telluric acid crystals, in spite of being dried over phosphoric oxide for three months, still contain occluded water, a supposition which the writer, in an investigation which is to be published shortly, can fully confirm. Marckwald's work again places tellurium beyond iodine in the periodic classification.

W. R. Flint [9] has extended his investigation of the behaviour of tellurium chloride when precipitated by water. More than 1000 grams of the chloride, dissolved in a minimum quantity of hydrochloric acid, were added to four litres of boiling distilled water, the precipitated dioxide again dissolved in hydrochloric acid, and reprecipitated by water. After four such fractionations, the atomic weight of tellurium was determined, by converting the dioxide into the basic nitrate and igniting again to the dioxide. The mean of four concordant determinations gave 126·59, a whole unit below the accepted number. Continuing the fractionation until it had been repeated ten times, 23 grams of the dioxide were obtained, and seven determinations of the atomic weight gave a mean result of 124·32. The less hydrolysed fraction was precipitated by ammonia and ammonium acetate, the dioxide dissolved in hydrochloric acid, and precipitated by water. This process was repeated three times, and 10 grams of dioxide were obtained. On frac-

[6] *Ber.*, 1907, **40**, 4730 ; *A.*, 1908, ii, 33.

[7] H. B. Baker, *Chem. News*, 1908, **97**, 209 ; *A.*, 1908, ii, 483.

[8] W. Marckwald and A. Foizik, *Ber.*, 1910, **43**, 1710 ; *A.*, ii, 604.

[9] *Amer. J. Sci.*, 1910, [iv], **30**, 209 ; *A.*, ii, 845.

tionating this by adding ammonia to the boiling hydrochloric acid solution, 8 grams of an orange-coloured, crystalline substance, 2 grams of yellow crystals, and 0·1 gram of a pale green substance were obtained. These substances gave a black precipitate, as tellurium does, with stannous chloride, and tests made for copper, iron, tungsten, bismuth, and antimony gave negative results. No atomic weight determination was made with this less hydrolysable fraction. In dealing with the earlier paper in last year's report, it was shown that the mean atomic weight of the original tellurium as calculated from both fractions was 126·89. In the newer work the author has determined the atomic weight of the material before fractionation, and finds it to be 127·45. He concludes that the lowest number, 124·32, is the nearest approach which has yet been made to the atomic weight of the element. The work is of the greatest interest; if confirmed, it would remove one of what have been called "the three blots of Mendeléeff's scheme." The work reads most convincingly, and it seems to have been done with great care, but the large number of methods which have been unsuccessfully tried previously for the resolution of tellurium makes one cautious in accepting Flint's most striking results. A possibility of a mistake in the work seems to be the presence in his tellurium of two impurities, one of higher and one of lower equivalent, which would accumulate in the end fractions. The work is, for this reason, now being repeated by the writer in conjunction with Dr. A. Vernon Harcourt, Professor Marckwald having most generously lent for the purpose a large quantity of his highly purified telluric acid.

Molecular Weights.

Several researches have been described during the year on the solution of iodine in various solvents. The view of the difference between the violet and the brown solutions taken in last year's report, was that in the brown solutions combination had taken place between the iodine and the solvent, whilst the violet liquids were purely mixtures of iodine and the solvent. This view is, to some extent, supported by the work of P. Waentig,[10] although he concludes that in the violet solutions some association takes place. The work was mainly spectroscopic in character. On heating violet solutions, displacement took place towards the red end of the spectrum, that is, towards the position of the band in iodine vapour. On allowing the solution to cool, the original position of the band is regained. With many brown solutions, on the other hand, a permanent alteration of the absorption spectrum is observed. The author believes that since brown solutions in thiophen and liquid

[10] *Zeitsch. physikal. Chem.*, 1909, **68**, 513; *A.*, ii, 117.

sulphur dioxide become violet on heating, regaining their colour on cooling, there is only a difference of degree between the violet and the brown solutions. The heat of solution in different solvents is negative, except in pyridine, and from this last solution a compound, PyI_2, has been isolated, but the heat absorption is much less for brown than for violet solutions. The partial pressures of the solutions indicate that, even at the boiling point, there is considerable association between iodine and the solvent in brown solutions. The experiments recorded above, however, may be reconciled with a different hypothesis. Amann[11] has submitted solutions of iodine to observation with the ultramicroscope. He finds that the violet solutions in carbon disulphide, carbon tetrachloride, and chloroform, and the yellowish-brown solutions in aniline, dimethylaniline, and phenol are devoid of ultramicroscopic particles. On the other hand, large numbers of particles are seen in the brown solutions in ethyl and methyl alcohols, acetone, and aqueous sodium iodide, and also in the violet solutions given by various petroleums. Benzene, toluene, acetic acid, and water give solutions which contain few particles. The ultramicroscopic character of many of the solutions is largely altered when the solution is exposed to light. On exposure of benzene and toluene solutions, large numbers of particles are formed with great rapidity, and the colour changes to yellowish-brown. In the dark these solutions regain their violet colour, and the ultramicroscopic particles disappear.

The molecular weights of neon and helium have been redetermined by Watson.[12] A quantity of a gas rich in these two constituents was given by M. Claude to Sir W. Ramsay, and served as the source of the purified gases used in the experiments. The use of diffusion through a heated silica tube was first tried for separating the two gases, since it was known that helium passed through such a tube. The rate of passage of the gas through the tube, heated to 1200°, was extremely slow, and it was also found to be mixed with neon. The process was therefore abandoned, and Dewar's process of fractionating by means of charcoal cooled by liquid air was used. The molecular weight of neon was found to be 20·20, and that of helium, 3·994.

Combustion.

No one has done so much to throw light on the processes which take place when substances burn as Professor H. B. Dixon. From the time of Boyle, many great names have been connected with the study of this part of the subject, but it may safely be said that no researches have penetrated so deeply into the nature of the chemical

[11] *Zeitsch. Chem. Ind. Kolloide*, 1910, **6**, 235; *A.*, ii, 496.
[12] *Trans.*, 1910, **97**, 810.

processes involved, as those which are associated with the name of the President of the Society. The researches are seen to be of the greater importance when it is considered that they involve the study of the simplest of all chemical changes, and it is here, if anywhere, that the chemist will attain a knowledge of what is the nature of the force of chemical attraction. In the latest of his investigations, which formed the subject of the Presidential Address,[13] Professor Dixon describes experiments which confirm the fact that water vapour is necessary to initiate the reaction of hydrogen and oxygen at comparatively low temperatures. In the explosion of these gases, however, his experiments lead him to the belief that the action takes place directly. The evidence for these views must seem to all chemists extremely strong, and there is nothing inconsistent in the idea that in the great rapidity of movement, and the intense local energy that is developed in a gaseous explosion, the splitting off of electrons, or whatever other cause is effective in the chemical union, may take place without the intermediary which is apparently necessary when the union is less violent. It seems to the writer that we shall never know the essential facts of a gaseous explosion without a more complete study of the nature of the electric spark, which is perhaps the least complicated of the many ways in which an explosion may be originated. One question which remains to be settled is whether the difference of action between a strong and a weak spark, which is so very manifest in an explosive mixture, is in any way connected with particles disrupted from the electrodes, or whether the effect is due entirely to the greater heat and light developed in the stronger spark. Dixon mentions his many experiments made to find out if sparks could be passed in dried electrolytic gas; whatever the nature of the metallic electrodes, an explosion always resulted, but it may be recalled that extremely minute and yet visible electric sparks have been passed in the mixture without apparent result.[14] Dixon proceeds to discuss the three arguments which have been adduced in favour of the hypothesis that hydrogen peroxide is the first product in the flame of hydrogen and oxygen: (1) that hydrogen peroxide is found in the water rapidly condensed from such a flame; (2) that the mixture of equal volumes of the gases is more sensitive to the action of a spark; (3) that the mixture in equal volumes has a lower ignition-point than any other mixture. With regard to the isolation of hydrogen peroxide from the products of combustion of hydrogen in oxygen, Dixon suggests that, since ozone is also produced,[15] it may easily be that an atom of oxygen may combine

[13] *Trans.*, 1910, **97**, 661.
[14] H. B. Baker, *ibid.*, 1902, **81**, 404.
[15] Manchot, *Ber.*, 1909, **42**, 3948; *A.*, 1909, ii, 993.

with a molecule of water previously formed, and that the hydrogen peroxide is produced in this way, and not by direct union. When nitrous oxide is substituted for oxygen, only a trace of hydrogen peroxide is formed, and although the analogy of the two experiments cannot be pushed too far, in the case of the nitrous oxide there is a less chance of splitting off an oxygen atom. In the explosion of hydrogen and oxygen, no trace of hydrogen peroxide has been detected, although one would think that if that substance were the primary product of the union of the gases, no more favourable circumstances could exist for the formation and continued existence of so endothermic a compound. The high temperature and sudden cooling behind the flame would be precisely the conditions which one would think necessary for a high yield of hydrogen peroxide. With regard to the second argument, it has been shown by Coward that the mixture of equal volumes of hydrogen and oxygen is not the most sensitive to the spark, since further addition of oxygen increases the sensitiveness. The third argument, that the mixture of hydrogen and oxygen in equal volumes has a lower ignition-point than any other mixture, rests mainly on the experiments of Falk.[16] In these, the ignition-point of the gaseous mixture was determined by finding the compression caused by a moving piston necessary to cause the gases to unite. Falk assumes that when the piston reaches the point, it is instantaneously stopped. Dixon, on the other hand, by photographing the explosion produced by adiabatic compression on a rapidly moving film, has shown that the equimolecular mixture of oxygen and hydrogen takes an appreciable time for combination. The piston therefore moves while the explosion is taking place. By an ingenious arrangement, Dixon was able to stop the piston at the point when the explosion just began, and the experiments showed that there was a progressive decrease in the temperature of ignition of mixtures of hydrogen and oxygen from $3H_2 + O_2$ to $H_2 + 4O_2$. Hence the last argument for the direct formation of hydrogen peroxide in the flame falls to the ground.

From what has been said above, it is obvious that the problem requires help from the physical side. Physicists are, however, too apt to neglect the chemical aspect of their studies and, in investigating these physico-chemical problems, to look upon the purity of materials as an unimportant factor. A striking exception to this is found in the work of the Rev. P. J. Kirkby. His work on the catalytic action of platinum on the union of hydrogen and oxygen at low pressures,[17] and on the chemical action of the

[16] *J. Amer. Chem. Soc.*, 1906, **28**, 1517; 1907, **29**, 1536; *A.*, 1907, ii, 18, 946.
[17] *Phil. Mag.*, 1905, [vi], **10**, 467; *A.*, 1905, ii, 695.

electric discharge,[18] is quite exceptional in the care that has been taken to use the best and most refined chemical methods. The theory put forward in the latter paper assumes that the chemical action is due to molecular dissociation effected by the collisions of gaseous ions constituting the current with the molecules of the gas; the atoms are thus set free to enter into new combinations. An account is given of experiments designed to determine both the number of molecules of water formed by the passage of the atomic charge through 1 cm. of the positive columns of various discharges in electrolytic gas, and also the electric force within these columns. The experiments support the hypothesis that the water vapour is formed by the collision of an *atom* of oxygen and a *molecule* of hydrogen. The experiments also prove that dissociated atoms of oxygen are not charged electrically. The latter result is confirmed by recent experiments of the writer with F. E. Thomas, which show there is no leakage of electricity in a tube in which ozone is undergoing dissociation.

The examination of the electrical conductivity of flames is likely to give considerable help to the understanding of chemical combination in these circumstances. A considerable amount of work in this direction has been accomplished by Haber and his students. It is shown [19] that with a large supply of air the electrical conductivity of the inner green cone of the Bunsen burner is comparatively high. Epstein and Krassa [20] show that as electrodes are gradually lowered into a flame from the top, the electrical conductivity increases regularly, but there is a sudden increase when the luminous zone is reached. When the proportion of oxygen, mixed with the coal gas, is gradually diminished, the change in conductivity on reaching the luminous zone is less sudden. There is thus a close connexion between the luminosity of a flame (separation of free carbon) and the electrical conductivity. The writer cannot help feeling that there is some connexion between this fact just established and the fact that all the gases, on the combustion of which the absence of water seems to have no influence, are compounds of carbon (CS_2, C_2N_2, CH_4, C_2H_4, C_2H_6).

Reference must be made here to a most admirable report on Combustion by W. A. Bone.[21] The facts are most clearly set forth, and it should be in the hands, not only of all students, but of all chemists.

[18] Compare *Chem. News*, 1910, **102**, 299.
[19] F. Haber and B. S. Lacy, *Zeitsch. physikal. Chem.*, 1909, **68**, 726; *A.*, ii, 122.
[20] *Ibid.*, 1910, **71**, 28; *A.*, ii, 202.
[21] *Brit. Assoc. Report*, 1910. Reprinted in *Chem. News*, 1910, **102**, 259.

Solution and Water of Crystallisation.

An interesting paper on the solubility of some sparingly soluble salts has been published by Melcher.[22] The salts used were silver chloride, barium sulphate, and calcium sulphate. The solubility was determined by a conductivity method at 18°, 50°, 156°, and 218°, a platinum-lined bomb being used. The solubilities, in milli-equivalents per litre, of the first two salts were: silver chloride, 0·0105 at 18°, 0·0365 at 50°, and 0·0147 at 100°; barium sulphate, 0·0190 at 18°, 0·0212 at 25°, 0·0288 at 50°, 0·0334 at 100°. The solubility of calcium sulphate was different according to the variety of salt used as the starting point, thus affording another example of what Mendeléeff imagined to be an argument against the dissociation theory of solutions. Thus, gypsum gave a solubility of 29·5 at 18°, 30·0 at 50°, 23·3 at 100°; soluble anhydrite gave a solubility of 22·8 at 100° and 6·4 at 156°; anhydrite gave a solubility of 9·2 at 100°, 2·7 at 156°, and 0·7 at 218°.

The solubility of calcium carbonate in solutions of ammonium salts may often be of serious consideration in quantitative analysis. It is pointed out by Rindell[23] that, at 25°, the solubility of calcium carbonate in solutions containing 500 millimols. of the following salts per litre is, for ammonium chloride, 5·008, ammonium nitrate, 5·267, and triammonium citrate, 66·87. It is also shown that the precipitation of calcium oxalates in presence of ammonium salts, especially the citrate, is not complete.

Further investigations on the chemical behaviour of substances dissolved in solvents other than water have been made by A. Naumann.[24] In ethyl acetate solution, ammonia and hydrogen sulphide react to form white crystals of ammonium hydrosulphide. With excess of hydrogen sulphide, yellow polysulphide is formed. Ammonium chloride is precipitated when a solution of ammonia in ethyl acetate is treated with hydrogen chloride. Mercuric chloride is easily soluble in ethyl acetate, and hydrogen sulphide gives with the solution a precipitate of the composition $HgCl_2,2HgS$, whilst ammonia precipitates the substance $HgCl_2,2NH_3$. The boiling-point method gives 254·9—269·2 for the molecular weight of mercuric chloride in ethyl acetate solution. The bromide and iodide of mercury behave in a similar manner, although their solubility is less. Potassium mercuri-iodide in ethyl acetate solution gives no precipitate with either ammonia or hydrogen sulphide. Stannous chloride is converted into a stannic salt by both chlorine and

[22] *J. Amer. Chem. Soc.*, 1910, **32**, 50; *A.*, ii, 293.
[23] *Zeitsch. physikal. Chem.*, 1910, **70**, 452; *A.*, ii, 294.
[24] *Ber.*, 1910, **43**, 313; *A.*, ii, 211.

bromine, and even when present in excess reduces mercuric chloride only to mercurous chloride. The experiments are of importance as regards the dissociation theory, especially as it is shown that the molecular weights of all the salts determined are practically normal.

A remarkable series of experiments has been made on potassium mercuri-iodide by J. E. Marsh.[25] The salt $KHgI_3,H_2O$ crystallises well from alcohol; it is soluble in a very small quantity of water, but is decomposed by excess. In a sealed tube, it melts in its water of crystallisation at 119°. In ether which has been shaken up with water, the salt is completely soluble, but, on warming, crystals of the monohydrate separate out. When potassium iodide and mercuric iodide are allowed to remain with undried ether, the monohydrated double salt is formed only after some weeks. If, however, ether which has been dried by sodium is used, and consequently water is not available, the two mixed salts gradually pass into solution, and a heavy yellow liquid is formed, which contains one molecule of the mercuri-iodide and four molecules of ether. Any excess of ether above the amount required for the formation of the compound floats above the heavy liquid. If the ether is not present in sufficient quantity to form the compound, part of the solid salts are left undissolved. The compound $KHgI_3,4Et_2O$, on being exposed to dried air, loses ether and becomes crystalline, and the author believes that the crystals have the composition $KHgI_3,3Et_2O$. The behaviour of the heavy liquid with small quantities of water exhibits many interesting phenomena. Many similar compounds containing ether are described, and the fact that the ether apparently exists in definite molecular proportions, without necessarily forming crystals, exhibits a type of association which seems to be intermediate between that of water of crystallisation and definite chemical combination.

The number and composition of hydrates of salts have been studied by Cumming.[26] Attention is drawn to the doubt which exists about the hydrates of even a salt like sodium carbonate, of which no fewer than twelve have been described, although other workers have asserted that only two or three have a separate existence. Defects are pointed out which are inherent to both the solubility method and the calorimetric method of identifying hydrates, and it is shown that the vapour-pressure method is capable of giving very satisfactory results. The basis of the method is an observation of Andreae,[27] that if three hydrates of a salt be placed in a closed vessel, the highest will lose water to the lowest until there are only two hydrates in the system. The principle was used by Walker

25 *Trans.*, 1910, **97**, 2297. 26 *Ibid.*, 593.
27 *Zeitsch. physikal. Chem.*, 1891, **7**, 241 ; *A.*, 1891, 781.

and Beveridge[28] in the isolation of *p*-toluidine monohydrate. The author applies it to the investigation of the hydrates of sodium carbonate. The monohydrate was first prepared by placing in the same desiccator a large quantity of anhydrous salt and a small, weighed quantity of the decahydrate. In three days, the loss in weight showed that it had been converted into the monohydrate, and after nine days more no further loss in weight was observed. To prepare the next higher hydrate, a mixture of anhydrous sodium carbonate and its decahydrate was made in such a proportion that the mixture contained, as a whole, one molecule of sodium carbonate to one molecule of water. After keeping it in a closed space for three weeks, this mixture was used to dehydrate a weighed quantity of decahydrate, and it was found that in seven days the latter had lost almost exactly three molecules of water, and there was practically no further loss in three days more. No hydrate could be found by this method between the heptahydrate and the decahydrate. The reverse process was also attempted of forming the heptahydrate by exposing the anhydrous salt to an atmosphere in which a large quantity of a partly effloresced specimen of the decahydrate was also present. The hydration reached a point where 6·93 molecules of water were present to 1 molecule of the salt in ninety-six days, and no further increase in weight took place during a further exposure of one hundred and twenty days. The highest hydrate was similarly produced by exposure to an atmosphere containing a saturated solution of the salt. Only three hydrates therefore probably exist: Na_2CO_3,H_2O, $Na_2CO_3,7H_2O$, and $Na_2CO_3,10H_2O$.

A possible explanation of the larger number of hydrates of sodium carbonate which have been described is afforded by a further paper by Cumming.[29] A large specimen of sodium carbonate had been left to effloresce in a partly closed case for twenty years. By determining its loss on ignition only, it was thought to correspond roughly with the formula $Na_2CO_3,3H_2O$, but further investigation showed that it was really the sesquicarbonate, $Na_2CO_3,NaHCO_3,H_2O$. The author suggests that the crystals described as $Na_2CO_3,4H_2O$ were really the bicarbonate.

The action of calcium carbide on hydrated crystals has been investigated by Irvine Masson.[30] It was found that many salts were completely dehydrated by shaking them with excess of calcium carbide at the ordinary temperature. The acetylene evolved was measured over mercury in a manometer, and served as a means of estimating how much water had entered into reaction with the carbide. With some salts (those which have a high water-vapour

[28] *Trans.*, 1907, **91**, 1797.
[29] *Chem. News*, 1910, **102**, 311.
[30] *Trans.*, 1910, **97**, 851.

tension), the action is very rapid, about half a gram being dehydrated in thirty seconds. In several cases the action only begins at 100°, and in others incomplete dehydration is found even at temperatures as high as 170°, even where there is no question, as in the case of barium chloride, $BaCl_2,2H_2O$, of the existence of what Graham termed "water of constitution." With other salts, such as copper sulphate, $CuSO_4,5H_2O$, the amount of true water of crystallisation is sharply defined, 4·02 molecules entering into reaction as the temperature is raised to 100°. An interesting example is oxalic acid, $C_2H_2O_4,2H_2O$, the water of which reacted in the cold, without chemical action taking place between the oxalic acid and the calcium hydroxide. The method may have some value in the study of the method of combination of water of crystallisation with salts.

The Rusting of Iron.

The attempts which have been made towards the solution of the problem of the cause of the rusting of iron have been very numerous, and the additional facts brought to light during the year make it possible to give a useful summary of our knowledge of the subject. Until comparatively recently, the action was supposed to be one of direct oxidation. Crace-Calvert[31] attributed the action to the presence of carbonic acid. Crum Brown[32] supported this idea, imagining ferrous carbonate and hydrogen to be the first products; the hydrogen was supposed to combine with the oxygen dissolved in the water, and the ferrous carbonate oxidised to rust by the same agency; the carbon dioxide liberated in the latter action would be then capable of recommencing the cycle of operations, and so the rusting would proceed indefinitely. Traube,[33] having shown that hydrogen dioxide was produced during the action of water on several metals, imagined that this substance was also a precursor of the rusting of iron, although he was unable to detect its presence in water in which rusting had taken place. Dunstan, Jowett, and Goulding[34] considered that their experiments proved that rusting would take place in absence of carbon dioxide, and they supported strongly the view held by Traube. Moody,[35] however, finally disposed of the hydrogen peroxide hypothesis by showing that bright iron would go on catalytically decomposing redistilled hydrogen dioxide for some weeks without any rusting taking place. The hydrogen dioxide must, in fact, have inhibited the action, since all

[31] *Manchester Lit. Phil. Mem.*, 1871, **5**, 104.
[32] *J. Iron and Steel Inst.*, 1888, **11**, 129.
[33] *Ber.*, 1885, **18**, 1877; *A.*, 1885, 1105.
[34] *Trans.*, 1905, **87**, 1548.
[35] *Ibid.*, 1906, **89**, 720.

the conditions for rapid rusting were fulfilled, the oxygen being even in the "nascent" state. Moody further pointed out that the boiling of water for a short time would not get rid of the last traces of carbon dioxide. By very carefully purifying water and air, he was able to keep the three substances, air, water, and iron, in contact for a prolonged period without rusting taking place. Sir William Tilden,[36] however, objected to Moody's experiments on the ground that in purifying the surface of the iron he had used a dilute solution of chromic acid, and hence rendered the iron passive. Repeating the experiments with great care, Tilden drew the conclusion that commercial iron would always rust in presence of water and air. It should be pointed out, however, that Moody showed that if a little carbon dioxide was allowed to pass into the tube containing the bright iron in the purified water, rusting at once took place. Many attempts have been made by the writer to make iron passive to ordinary water by treatment with dilute chromic acid, but all have been unsuccessful. The writer is of opinion therefore that Moody must be given the credit of having proved that water, iron, and air, when in a purified condition, do not interact. In 1903 Whitney[37] propounded a theory of rusting, according to which an acid is not necessary. Since the purest water yet attained is slightly dissociated, metallic iron would pass into solution as ferrous hydroxide. Tilden supports the theory, supposing that either the impurities or even the harder parts of the metal form couples with the purer iron. Attention may be drawn to the fact, which strongly supports Tilden's last suggestion, that in almost all cases rust forms on iron in spots, which only slowly extend over the surface of the bright metal. Walker, Cederholm, and Bent[38] believed that they had confirmed Whitney's contention that iron will dissolve to an appreciable extent in pure water, but as Friend has pointed out, their result is probably vitiated by the fact that traces of carbon dioxide were not altogether excluded by their method of working. Friend,[39] who has made many experiments on the subject, also shows that the bacterial explanation of rusting is untenable, and confirms Moody's work. The latest investigation by Lambert and Thomson[40] contains by far the most elaborate and careful work that has been done on the subject. It is perhaps not generally recognised that work of this kind demands an amount of care and precaution very far beyond what would be thought necessary in, for instance, a good atomic-weight determination.

[36] *Trans.*, 1908, **93**, 1356.
[37] *J. Amer. Chem. Soc.*, 1903, **25**, 394; *A.*, 1903, ii, 430.
[38] *Ibid.*, 1907, **29**, 1251; *A.*, 1907, ii, 875.
[39] *J. Iron and Steel Inst.*, 1908, **77**, i, 2, 5; *A.*, 1908, ii, 698.
[40] *Trans.*, 1910, **97**, 2426.

Iron was obtained of a very high degree of purity by electrolysing purified ferric chloride, using iridium electrodes. The iron deposited was converted into ferric nitrate by means of very pure nitric acid, and this salt repeatedly crystallised from nitric acid. The salt was ignited in an iridium boat, and reduced to metal in hydrogen, obtained by the only method which gives the gas in anything like a pure condition, namely, the electrolysis of a solution of carefully purified barium hydroxide. The iron was contained in a silica test-tube, which was enclosed in a tube of Jena glass. Water was distilled from a dilute solution of barium hydroxide, without actual boiling, through a trap to prevent any possibility of the hydroxide being carried over. The experiment was so arranged that the water vapour which was ultimately condensed on to the iron was condensed only on silica. Oxygen, prepared by the electrolysis of barium hydroxide, which has been shown by many workers to be free from ozone and other impurities, was admitted to the tube containing the iron. In these circumstances the three substances, iron, water, and oxygen, were found to be capable of contact without chemical action for some months. Moody's contention therefore is amply confirmed, but it must not be considered that the question is finally set at rest. In some of Lambert and Thomson's experiments, rusting undoubtedly took place, although carbon dioxide and other impurities were excluded. For the sake of comparison, mention may be made here of recent experiments on a similar subject.[41] It has been shown that water can be obtained by careful distillation in such a state that it exhibits scarcely any action on sodium amalgam. The purity of this water, measured by its electrical conductivity, is not of a very high order, and yet it exhibits a chemical inertness greater than that of water, which, measured by the same standard, is considerably purer. The writer suggests, with some diffidence, the hypothesis that it is possible that oxygen in solution may be, in some circumstances, dissociated, and in others not dissociated, and that in the latter case only it exhibits chemical activity towards metals. Experiments now in progress should give a definite decision on this point.

Metals and Alloys.

Small quantities of strontium have been prepared in a crystalline condition by Guntz and Galliot.[42] Anhydrous strontium oxide, mixed with the calculated amount of powdered aluminium, was heated in a steel tube surrounded by an exhausted porcelain tube. A temperature of 1000° was maintained for four hours, and, on

[41] H. B. Baker, *Trans. Faraday Soc.*, 1910, **6**, 120.
[42] *Compt. rend.*, 1910, **151**, 813 ; *A.*, ii, 1064.

cooling, silver-white crystals, containing 99·4 per cent. of the metal, were obtained.

Metallic strontium has been prepared in quantity by B. L. Glascock[43] by the electrolysis of fused strontium chloride. Very considerable trouble was experienced on account of the formation of carbide and an iron alloy from the electrodes, and also because the metal does not, like calcium, adhere to the cathode. Strontium is more oxidisable than calcium, and so soft that it can easily be cut with a knife. It reacts with water, methyl and ethyl alcohols, and acetoacetic and malonic esters with evolution of hydrogen. Strontium burns in carbon dioxide as readily as it does in air, forming some carbide and free carbon. The hydride is formed by direct union with hydrogen. Analysis of the metal showed that it contained 1·5 per cent. of impurity. The specific heat was found to be 0·0742, and conforms to Dulong and Petit's law, giving 6·5 as the atomic heat.

Metallic radium has been prepared by Mme. Curie and A. Debierne.[44] The method was based on the preparation of the amalgam and subsequent expulsion of the mercury. The amalgam was produced by the electrolysis of a solution of radium chloride, using a mercury cathode and an anode of platinum-iridium. The weight of radium chloride used was 0·106 gram, and that of the mercury about 10 grams; the amount of radium chloride left in the solution was 0·0085 gram. The amalgam was quite liquid, whereas a barium amalgam prepared under the same conditions contained crystals. Radium amalgam decomposes water, and changes rapidly in the air. After drying, it was rapidly transferred to an iron boat, which was heated in a silica tube in hydrogen. The heating must be performed with very great care, since, if the mercury is allowed to boil, some of the radium is lost. The temperature was determined by a thermoelectric junction connected to the boat. It was found that hydrogen, purified and dried by the ordinary methods, attacked the amalgam and the metal. The authors state that by passing the gas through a red-hot platinum tube, they obtained "perfectly pure hydrogen." Most of the mercury was distilled off at 270°, and the temperature was raised. The pressure of the hydrogen was increased at the same time, in order to prevent the mercury boiling. At 400° the amalgam was solid, but melted at a higher temperature. At 700° no further volatilisation of mercury was noticed, but radium began to vaporise and attack the silica tube. The boat then contained a bright metal, which melted sharply at 700°. It was difficult to detach the metal from the iron.

[43] *J. Amer. Chem. Soc.*, 1910, **32**, 10; *A.*, ii, 954.

[44] *Compt. rend.*, 1910, **151**, 523; *A.*, ii, 816.

Metallic radium rapidly alters in air, becoming black, probably owing to the formation of a nitride. When a particle of the metal was dropped on to white paper, blackening was produced as if the paper was burnt. When the metal is placed in water, energetic decomposition takes place, and most of it dissolves, showing that the hydroxide is soluble. The insoluble residue is probably nitride, and since it is completely soluble in dilute hydrochloric acid, it is certain that the mercury had been completely removed. Since the metal is more volatile than barium, the authors propose to use the fractional sublimation of the metals in a vacuum as a means of obtaining pure radium from the mixed radium barium preparations.

This has been shown to be feasible by Ebler,[45] although a very much smaller quantity of the radium bromide was used. One milligram of radium barium bromide, containing 9 per cent. of radium bromide, was converted into radium barium azoimide. This was heated in a very small glass tube, contained in a larger tube, which was kept vacuous. After being kept for some hours at a temperature of 180—250°, a shining metallic mirror was formed, which was sealed off from the residue, and found to contain 73 per cent. of the radium in the original substance used.

Prandtl and Bleyer[46] have investigated the production of metallic vanadium by the thermite process. When vanadium pentoxide and aluminium are fired in a magnesia crucible, reduction only takes place to a lower oxide. Metallic calcium mixed with the aluminium produces vanadium, but the impurities in commercial calcium render the resulting vanadium impure. The authors find, however, that a much purer metal is obtained by using a mixture of 100 parts of vanadium pentoxide, 49·5 parts of aluminium, and 20 parts of calcium fluoride.

The production of metallic tungsten has been studied by L. Weiss.[47] The thermite process with wolframite is very violent, but it can be made manageable by using deficiency of aluminium. The resulting metal contains 90 per cent. of tungsten, and part of the impurity, consisting mainly of manganese and iron, can be removed by hydrochloric acid. Electrolysis of tungstic acid fused with cryolite gives a metal containing 96 per cent. of tungsten, but it is not coherent. The best product, which contained 99 per cent. of tungsten, was obtained by fusing tungsten trisulphide with lime. The metal is not magnetic, and is to some extent malleable. It is only slowly attacked by aqua regia, and it can only be brought into solution by a mixture of nitric and hydrofluoric acids.

In a research on zirconium by L. Weiss and E. Neumann,[48] the

[45] *Ber.*, 1910, **43**, 2613 ; *A.*, ii, 1024. [46] *Ibid.*, 2602 ; *A.*, ii, 1075.

[47] *Zeitsch. anorg. Chem.*, 1910, **65**, 279 ; *A.*, ii, 216.

[48] *Ibid.*, 248 ; *A.*, ii, 217.

metal was prepared by the ordinary methods, and it was found that when the powder was compressed into rods by pressure, it conducted electricity. Previous observers had stated that the metal is a non-conductor. The authors confirm the existence of zirconium hydride, first prepared by Winkler.[49] The hydride has been prepared by direct union of the metal with hydrogen, and burns in oxygen, forming Zr_2O_3.

The alloys of magnesium and gold have been investigated by Urazoff.[50] They were obtained by heating the constituent metals together in a graphite crucible enclosed in an iron vessel with a screw top. Combination took place at 700°. Four compounds were indicated by the freezing-point curve, namely, AuMg, with a maximum at 1150°, $AuMg_2$, with a maximum at 788°, Au_2Mg_5, with a break in the curve at 798°, and $AuMg_3$, with a maximum at 818°.

Continuing the researches published last year, Charpy and Bonnerot[51] have applied more rigorous methods in order to find if the cementation of iron takes place when carbonising gases are eliminated as far as possible. Soft Martin steel, containing practically only iron, carbon, and a little manganese, as well as varieties of carbon, sugar-charcoal, purified graphite, and white diamonds, were heated in separate tubes to 1000° in a vacuum to get rid of occluded gases. The iron and carbon were then brought together, and to purify them still further were heated to 700° in a vacuum. The temperature was then raised to 1000° and kept so for several hours, the vacuum pump being continually worked. In these circumstances no cementation took place with any of the varieties of carbon. The authors have not succeeded in compressing the carbon and iron together in a high vacuum, but it is probable that in view of their experiments of last year, cementation would not have been effected by the increased pressure.

It has been noticed that fracture in steel often takes place at an area lying between two parts where segregation has taken place, the proportion of carbon being different on the two sides of the fracture. It was found by Giolitti and Tavanti[52] that such segregation could be avoided by a process of cementation. A current of carbon dioxide was passed over purified carbon, and then over the steel, both heated to a high temperature. In these circumstances, the outer layers of steel, at all events, receive an even distribution of carbon, and there is no abrupt change of high to low carbon steel.

[49] *Ber.*, 1890, **24**, 888; *A.*, 1890, 1372.
[50] *Zeitsch. anorg. Chem.*, 1909, **64**, 375; *A.*, ii, 43.
[51] *Compt. rend.*, 1910, **150**, 173; *A.*, ii, 215.
[52] *Atti R. Accad. Sci. Torino*, 1910, **45**, 539; *A.*, ii, 780.

The conditions which determine the composition of electro-deposited alloys have been investigated by Field.[53] The effect on the composition of brass, electrolytically deposited from cyanide solutions, was determined when the following conditions were varied: (*a*) composition of the solution; (*b*) strength of the solution; (*c*) temperature; (*d*) current density; (*e*) presence of free cyanide. It was found that, in absence of free cyanide, copper was the more easily deposited of the two metals when they were present in about equal proportions. In the same circumstances, increase of current density increases the percentage of zinc deposited, and a similar effect is produced by diluting the solution. Rise in temperature, on the other hand, increases the proportion of copper, and this is also the case if free cyanide is introduced. In a further paper,[54] the author has examined the co-deposition of silver and copper, which he finds only takes place within very narrow ranges of concentration. From the sulphates and nitrates, silver is deposited alone, even when a very large quantity of copper is present. The deposition of copper is promoted by diminution of the relative amount of silver, the use of cyanide solutions, the increase of current density, and the lowering of the temperature.

Some work has been done on the amalgams of mercury and silver by H. Chapman Jones.[55] They were prepared by the preparation of double salts of the metals, or of a mixture of salts in molecular proportions, and subsequent reduction by means of sodium sulphite or ferrous oxalate. The amalgam AgHg, prepared by the reduction of $AgHgCl_2$, had a specific gravity of 12·80; if no contraction had taken place, the calculated specific gravity would be 12·29. Joule[56] obtained an amalgam by direct union of the metals with a specific gravity of 14·68.

The solubility of gases in metals and alloys has been the subject of an extended series of investigations by Sieverts and his assistants.[57] The metals were heated in vessels of porcelain. The authors find a result which will be surprising, and, if it can be confirmed, very welcome to chemists, that Meissen biscuit porcelain is impenetrable to hydrogen at 1650°, and that vessels of this material will remain vacuous up to 1400°. An electric furnace was used for the heating, temperatures being estimated by means of a Wanner optical pyrometer. It has been proved that hydrogen is not absorbed by silver, either in the solid or the melted condition, and this is true also for zinc, cadmium, thallium, tin, lead, antimony, bismuth and

[53] *Trans. Faraday Soc.*, 1909, **5**, 172; *A.*, ii, 38.

[54] *Ibid.*, 1910, **6**, 1; *A.*, ii, 851.

[55] *Trans.*, 1910, **97**, 336.

[56] *Journ. Chem. Soc.*, 1863, **16**, 383.

[57] *Zeitsch. physikal. Chem.*, 1909, **68**, 115; *A.*, 1909, ii, 1004; *Ber.*, 1910, **43**, 893; *A.*, ii, 410; *Zeitsch. physikal. Chem.*, 1910, **74**, 277; *A.*, ii, 851.

gold. Hydrogen dissolves in copper both when it is solid and when it is fused. At constant pressure, the solubility in solid copper increases in a linear manner as the temperature rises; at the melting point there is a sudden increase in solubility, and the solubility then increases linearly up to 1500°. At 623°, 100 grams of copper dissolve 0·08 milligram of hydrogen, so that the earlier determination of the atomic weight of hydrogen must have been slightly affected by this cause. At constant temperature, the amount of hydrogen absorbed by fused copper is proportional to the square root of the pressure.

The solubility of hydrogen in solid palladium is stated to be practically independent of the temperature, a statement which is contrary to the experience of other workers. When the palladium is melted, there is a sudden fall in the solubility of hydrogen. The solubility of hydrogen in copper is not affected when the metal is alloyed with silver, it is increased by alloying with nickel or platinum, and it is diminished by alloying with gold, tin, or aluminium.

Sulphur dioxide is insoluble in solid copper, but dissolves to a considerable amount when the metal is fused, and the solubility increases when the temperature rises. It is remarkable that, as with hydrogen, the solubility is proportional to the square root of the pressure, since the ordinary explanation of dissociation of the molecule of hydrogen can scarcely be imagined to hold in the case of sulphur dioxide.

The experimental number for the solubility of oxygen in molten silver obtained by Sieverts has been confirmed by Donnan and Shaw.[58] They find that for 10 grams of silver, 20·5 c.c. of oxygen (measured at 0° and 760 mm.) are absorbed at 1020°. The authors calculate that the freezing point of silver saturated with oxygen should be lowered by 10·4°; the actual lowering is only 7°.

Group I.

Purists will no doubt object to the use of the term "dry nascent hydrogen" used in a very interesting series of papers by Vournasos.[59] The reducing action of sodium formate at about 400° has been applied to the formation of the hydrides of sulphur, phosphorus, and arsenic, the vapour of the element being passed over the heated formate. By mixing sodium antimonite with the sodium formate, stibine was formed; hydrogen boride and hydrogen silicide are likewise produced in small quantity when boron

[58] *J. Soc. Chem. Ind.*, 1910, **29**, 987; *A.*, ii, 844.

[59] *Compt. rend.*, 1910, **150**, 464; *A.*, ii, 286; *Ber.*, 1910, **43**, 2264; *A.*, ii, 951; *Ibid.*, 2272; *A.*, ii, 948.

and silicon are heated with the formate. Hydrogen selenide and hydrogen telluride are likewise produced, but, as is natural, the proportions of the hydrides are limited by their dissociation. Yields, however, of 12 to 17 per cent. by volume have been obtained of hydrogen arsenide. When sodium formate is heated with compounds containing two volatile constituents, such as the sulphides of phosphorus, arsenic, and antimony, or the phosphides of arsenic and antimony, mixtures of the corresponding hydrides are produced. Nitrides of the metals give ammonia, but silicides, borides, and carbides are not affected. The author recommends the process as a substitute for Marsh's test in certain circumstances; it is possible to detect 0·001 milligram of arsenic. The writer, in repeating some of these experiments, found that hydrogen containing a considerable percentage of boron hydride could be obtained by using powdered boron trioxide instead of boron.

The long and patient investigation of the photochemical inhibition of the interaction of hydrogen and chlorine has been continued by D. L. Chapman and P. S. MacMahon.[60] It has already been shown that oxygen, nitrogen chloride, and the gas formed by nitric oxide on moist chlorine (either nitrogen peroxide or nitrosyl chloride, according to the authors) act as inhibitors, while carbon dioxide, nitrogen, and nitrous oxide act only as diluents. Ozone and chlorine dioxide must now be added to the inhibitors, whilst chlorine monoxide, when free from oxygen, behaves as a neutral gas. Ozone was found to disappear quickly when left in the dark mixed with the hydrogen and chlorine.

A research of extreme difficulty has been accomplished by Wenz[61] on the determination of the velocity of sound in potassium vapour. The vapour was contained in a steel tube enclosed in one of porcelain, which was heated electrically to 850°. The steel tube was internally coated with silver. One end of the steel tube was closed by a plate of mica, which served for the vibrating resonance diaphragm, while a movable piston closed the other end. The distances between which resonant vibration could be observed were determined and compared with the corresponding lengths in air. The ratio of specific heats found was 1·77, and the conclusion is drawn from the experiments that potassium vapour is monatomic. The experiments thus confirm the measurements made of the vapour density of the metal.

An ammoniacal derivative of cuprous nitrate, $CuNO_3,2NH_3$, has been prepared by Sloan,[62] by allowing a solution of cupric nitrate in liquid ammonia to remain in contact with metallic copper. The substance is colourless, but it rapidly oxidises in the air.

[60] *Trans.*, 1910, **97**, 845. [61] *Ann. Physik*, 1910, [iv], **33**, 951; *A.*, ii, 1061.
[62] *J. Amer. Chem. Soc.*, 1910, **32**, 972; *A.*, ii, 852.

The colour of cupric salts has been the subject of an investigation by Rassenfosse.[63] Dissenting from the views of Donnan and Bassett,[64] the author believes the colour to depend on two factors: (*a*) the dissociation of the salt; (*b*) on its hydration. He adduces evidence to show that the colour changes of cupric chloride produced by (*a*) heating, (*b*) the addition of hydrochloric acid, (*c*) the addition of alcohol, are due to the formation of additive products of the salt, or by its dissociation. The addition of hydrochloric acid, for instance, to a cold saturated solution of cupric chloride produces a precipitate of a hydrate of cupric chloride, so that the colour change cannot be produced by dehydration. Zinc chloride, added to a green solution of cupric chloride in dilute hydrochloric acid, restores the blue colour, probably owing to the decomposition of the compound of cupric chloride and hydrogen chloride. Calcium chloride and magnesium chloride change the blue colour of an aqueous solution of cupric chloride to green, probably owing to the formation of compounds of the salts with the cupric chloride, since a mixture of saturated solutions of calcium and cupric chlorides deposits a mass of greenish-brown, deliquescent crystals of $2CuCl_2,CaCl_2,6H_2O$. When an aqueous solution of cupric chloride is heated, the colour changes to green, and hydrogen chloride is found in the aqueous vapour given off, and since the boiled solution has an increased resistance, the author concludes that it contains cupric hydroxide. The writer finds, however, that by heating a blue solution of cupric chloride in a sealed tube, the solution turns green on heating to 100°, and in this case there can be no loss of hydrogen chloride. When alcohol is added to a blue aqueous solution of cupric chloride, a green solution is formed, and this fact has been attributed to the dehydrating action of the alcohol. The author shows, however, that greenish-yellow crystals of $CuCl_2,2C_2H_5{\cdot}OH$ can be obtained from a solution of anhydrous cupric chloride in absolute alcohol. In connexion with this subject, an experiment performed in the writer's laboratory may be worth quoting. The blue colour of crystals of copper sulphate is usually attributed to the presence of cupric ions, and in spite of the comparative immobility of these ions, one would expect the crystal to show some electrical conductivity. A dry crystal, however, is found to be, on the contrary, a non-conductor to a very marked degree.

What are called crystalline photochlorides of silver have been prepared by Reinders[65] by allowing a solution of silver chloride in ammonia to crystallise in sunlight. The crystals were indigo blue in colour, and were found to contain about 1 per cent. of

[63] *Bull. Acad. roy. Belg.*, 1909, 1289; *A.*, ii, 210.
[64] *Trans.*, 1902, **81**, 939.
[65] *Chem. Weekblad*, 1910, **7**, 961; *A.*, ii, 1062.

colloidal silver. The crystals became reddish-brown on further exposure to light. There is little doubt that the crystals were the well-known $AgCl,2NH_3$. They rapidly colour in light, but the oxychloride of silver is not formed in this case, since it would be at once reduced to metallic silver by the ammonia. The fineness of division of the silver would obviously account for the differences in colour observed.

Group II.

The action of various hydrocarbons on metallic magnesium has been examined by Novák.[66] The products obtained in the different experiments were decomposed by water; the acetylene was estimated by absorption with cuprous chloride, and the allylene by silver nitrate. Two carbides, MgC_2 and Mg_2C_3, were found to be produced. When acetylene was passed over the heated metal, reaction began at 400°, MgC_2 being principally formed. As the temperature is raised, the amount of the carbide increases up to 490°, which is the most favourable temperature for its formation. At 460° the carbide Mg_2C_3 can be detected in the product, and the proportion increases up to 545°. At higher temperatures, carbon is set free, which at 700° increases so much as to block up the tube. The proportion of free carbon formed is greater in a steel tube than in a porcelain tube, as would be expected from the behaviour of acetylene when heated alone. In a porcelain tube, benzene and other hydrocarbons are produced, whilst in a steel tube the gas breaks up into carbon and hydrogen.

When methane is used instead of acetylene, the formation of free carbon is less when the temperature is as low as 560°, but at 780° the proportion of carbon is greater than when acetylene was employed. Pentane, octane, benzene, toluene, and the three xylenes gave results very similar to those obtained with methane. The prevailing reactions are supposed to be: at about 570°, $2MgC_2 = Mg_2C_3 + C$; and above 610°, $Mg_2C_3 = 2Mg + 3C$.

The research of R. L. Taylor[67] on bleaching powder is not concerned with the constitution so much as with the chemical behaviour of this substance. It consists of the determination of the relative amounts of chlorine and hypochlorous acid which are given off when bleaching powder is submitted to the action of air, with or without the presence of carbon dioxide. An ingenious method for estimating hypochlorous acid and chlorine in a mixed solution consisted in treating the solution with $N/10$-sodium arsenite. The equations:

$$As_2O_3 + 2Cl_2 + 2H_2O = As_2O_5 + 4HCl$$
$$As_2O_3 + 2HOCl = As_2O_5 + 2HCl$$

[66] *Zeitsch. physikal. Chem.*, 1910, **73**, 513; *A.*, ii, 778.
[67] *Trans.*, 1910, **97**, 2541.

show that, for the same amount of arsenite used, twice the amount of chloride is produced in the case of chlorine as in the case of hypochlorous acid. The arsenite is added in excess, and the solution divided into two parts. In one the excess of arsenite is determined by $N/10$-iodine solution, and in the other the chloride produced is estimated by silver nitrate. Carbon dioxide, passed over bleaching powder, was found to produce chlorine alone; if the carbon dioxide was previously dried by calcium chloride, no difference was found in the product, but the action was much retarded. Chlorine alone was also obtained when the bleaching powder was suspended in water, the action being much accelerated. Hence the author very reasonably concludes that the action of carbonic acid is similar to that of any other acid, and that it acts not only on the hypochlorite, liberating hypochlorous acid, but also on the chloride, forming hydrogen chloride, and that these two products, as usual, react to produce chlorine and water. It was asserted by Müller [68] that sodium chloride is decomposed by carbonic acid, the presence of hydrochloric acid in the solution being demonstrated by the decolorising of ultramarine. The writer can confirm the difficulty experienced by Taylor in observing this loss of colour. It can only be seen if the ultramarine is very dilute, and its colour compared with some of the untreated solution. Taylor demonstrates the fact of the formation of hydrochloric acid in a much more satisfactory way by the use of methyl-orange. Ordinary moist air passed over bleaching powder or through a solution of bleaching powder in water brings off at first hypochlorous acid and chlorine, and later almost pure chlorine. The deduction from this is that calcium hypochlorite undergoes slow hydrolysis, the hypochlorous acid being swept out with the chlorine, produced as above by the action of carbonic acid. The action of chlorine on alkalis is a reversible one, like that of bromine and iodine; if the free calcium hydroxide is removed, the reverse action proceeds. This explains the reason of the impossibility of preparing bleaching powder free from lime. The author adduces evidence to show that in the process of bleaching by the use of bleaching powder, the bleaching is mainly carried on by chlorine, and only to a slight extent by hypochlorous acid. The paper is an admirable one, of great theoretical as well as of practical interest.

The beautiful dark red compound produced by the action of bromine on calcium hydroxide, discovered originally by Berzelius, has been shown by L. G. Killby, in the writer's laboratory, to contain bromine in three forms, as bromide, hypobromite, and as bromine more loosely combined. The bromide and hypobromite are

[68] *Journ. Chem. Soc.*, 1870, **23**, 36.

in equivalent proportions, so that it contains a true bromine bleaching powder. The loosely combined bromine, to which the compound owes its red colour, is in some form of combination which has not yet been completely established, but it is probably present as a perbromide of calcium. A paper has been published by Wilks,[69] in which the absorption of bromine from carbon tetrachloride solution by calcium hydroxide is described. With weak solutions of bromine, the concentration of bromine in the lime increases with the concentration of the solution, pointing to the formation of an adsorption product. With more concentrated solutions of bromine, the quantity taken up is independent of the concentration and the ratio $Ca(OH)_2 : Br = 4{\cdot}42 : 1$, indicating the formation of a compound. With dry slaked lime, the ratio soon becomes constant at 14·9 : 1. The colour of the product increases until the constant concentration is reached.

Group III.

The substance known as crystalline boron always contains foreign elements derived from the substances used in its preparation. Biltz[70] has obtained yellow crystals by a thermite process, the mixture used being 50 grams of boron trioxide, 100 grams of aluminium, 75 grams of sulphur, and 2 grams of soot. After the action is over, the cooled mass is treated with water and with concentrated hydrochloric acid. The residue mainly consists of transparent, yellow crystals, which are quadratic, and mixed with them are black crystals. They are separated by flotation in methylene iodide. Both substances have been previously described; the yellow crystals obtained by Hampe[71] were said to have the formula $C_2B_{48}Al_3$. The author finds a slightly different composition, represented by the formula $C_2B_{44}Al_3$. There is no evidence as to the question of the crystals being a mixture or a compound.

Kohn-Abrest[72] has investigated the effect of heating metallic aluminium in a porcelain tube to 1100° in a vacuum. At first the metal volatilises readily, but after some time no further sublimation takes place. It is shown that a silicide of aluminium, Al_2Si, is produced, which, mixing with the metal, appears to raise its boiling point. The same effect is produced if the aluminium is isolated from the porcelain tube in a boat of graphite, which would seem to indicate that in one form or another the silicon must have passed through a vapour phase.

69 *Proc. Camb. Phil. Soc.*, 1910, **15**, 526; *A.*, ii, 1063.
70 *Ber.*, 1910, **43**, 297; *A.*, ii, 201.
71 *Annalen*, 1876, **183**, 75; *Journ. Chem. Soc.*, 1877, i, 273.
72 *Compt. rend.*, 1910, **150**, 185; *A.*, ii, 212.

Artificial sapphires were obtained fifty years ago by Deville and Caron, but their results could not be obtained by subsequent workers. Verneuil,[73] however, by heating alumina with 1·5 per cent. of magnetic oxide of iron and 0·5 per cent. of titanic acid in the reducing part of the oxyhydrogen flame, has produced crystals which are identical in properties with the natural stones. The colour is due to the presence of lower oxides of iron and titanium.

An interesting paper by Parsons and Evans[74] shows that when solutions of the alums are allowed to diffuse through a membrane, they are more or less completely separated, the authors believe, into the component simple sulphates. The chrome alums are more completely separated than the aluminium alums. It would seem possible, however, that it may be a question of hydrolysis of the sulphates of the triad metals, colloidal hydroxides being formed.

The most exact investigation which has yet been made of the compounds of scandium has been continued by one of the veteran Past Presidents of the Society, Sir William Crookes.[75] No less than twenty-two new salts, both of inorganic and organic acids, have been prepared and examined, with the minute care which the whole scientific world is accustomed to associate with the name of the author.

Group IV.

The direct synthesis of methane, which was indicated by Bone and Jerdan[76] and confirmed by Bone and Coward,[77] has again been the subject of very careful work. Pring,[78] taking great precautions as to the purity of materials, and using three varieties of carbon, graphite, gas-carbon, and sugar-charcoal, has confirmed the fact of the direct synthesis of methane, and has also shown that, whilst acetylene does produce methane at high temperatures, the methane produced at lower temperatures is produced by direct union of its elements. Bone and Coward, who had previously obtained 73 per cent. of the theoretical yield of methane when small quantities of carbon were used, have, by the use of improved apparatus, obtained almost the whole of the carbon as methane, three experiments giving 91, 95·6, and 95·8 per cent. respectively of the theoretical quantity. In the analysis of the hydrogen used, the authors state that the 0·007 per cent. of methane present in the gas is probably an exaggerated estimate. The writer, who has used much larger quantities in analysing the gas prepared by the same process, the electrolysis of barium hydroxide, found that no hydrocarbon

[73] *Compt. rend.*, 1910, **150**, 185 ; *A.*, ii, 212.
[74] *J. Amer. Chem. Soc.*, 1910, **32**, 1378 ; *A.*, ii, 1069.
[75] *Phil. Trans*, 1910, **210**, A, 359 ; *A.*, ii, 714.
[76] *Trans.*, 1897, **71**, 41 ; 1901, **79**, 1042.
[77] *Ibid.*, 1908, **93**, 1975 ; 1910, **97**, 1219.
[78] *Ibid.*, 1910, **97**, 498.

impurity at all could be detected in the gas. He is of opinion that the authors have adopted too low an estimate of the percentage of methane that they have obtained. If they have erred, however, it has been on the side of caution.

Some new metallic carbonyls are described in a paper [79] drawn up, just before his death, by the late Dr. Ludwig Mond. It is to this indefatigable worker that we owe the original discovery of these interesting substances, as well as the application of their formation to technical processes. Cobalt carbonyl, $Co(CO)_4$, is prepared from metal reduced from the oxide at 300° by a current of hydrogen. The metal is heated from 150—250° in carbon monoxide at 30—40 atmospheres pressure. The higher the pressure, the greater is the production of the compound up to 250 atmospheres, the highest pressure used. Fine orange crystals are produced, which melt without decomposition at 51°. Slow decomposition takes place at 60°. The molecular weight determined by the cryoscopic method showed the formula $Co_2(CO)_8$. A new compound, having the composition corresponding with the formula $Co(CO)_3$, is obtained by slow heating, but it is too sparingly soluble to get cryoscopic measurements. A hexacarbonyl of molybdenum has also been prepared at a minimum pressure of 150 atmospheres and a temperature of 200°. A carbonyl of ruthenium probably is capable of existence, but no similar compounds were obtained with manganese, chromium, tungsten, palladium, or rhodium.

The reaction between nickel carbonyl and thiocarbonyl chloride has been shown by Sir J. Dewar and H. O. Jones [80] to produce the long-sought-for carbon monosulphide, or a polymeride of this substance. It is a brown solid, which is not altered by dilute sulphuric acid. The concentrated acid gives a purplish-brown solution, which, on dilution, precipitates the monosulphide unchanged, a behaviour which recalls the similar action of concentrated sulphuric acid on sulphur, selenium, and tellurium. Concentrated nitric acid gives a red solution, which is only slowly changed by boiling. When heated to a low red heat in a vacuum, carbon and carbon disulphide are obtained. In continuation of the work,[81] the authors investigated the influence of the silent electrical discharge on carbon disulphide vapour at low pressures. When the gas produced was passed through a tube cooled by liquid air, carbon monosulphide was condensed with the unchanged disulphide. When the temperature is allowed to rise, the substance polymerises to form the brown substance described above. It is, however, not all decomposed when the mixture of the new gas with carbon disulphide is heated to 440°. So many different substances, prepared in so many different

[79] Mond, Hertz, and Cowap, *Trans.*, 1910, **97**, 798.
[80] *Proc. Roy. Soc.*, 1910, **83**, A, 408; *A.*, ii, 408. [81] *Ibid.*, 526; *A.*, ii, 408.

ways, have been described under the name of carbon monosulphide that it is highly satisfactory to get evidence of its real existence, such as is given in these two papers. Still a further research[82] by the same two authors describes the action of nickel carbonyl on carbon disulphide and other substances. It was proved by laborious investigations that carbon monosulphide was not produced in these actions. The effect of pressure on carbon monoxide has been studied by Briner and Wroczynski.[83] At 800 atmospheres pressure at the ordinary temperature, no change took place in the gas. At 320°, however, and under a pressure of 600 atmospheres, a contraction of 10 per cent. took place in twenty hours. Carbon dioxide was found, and a greyish-black deposit, which was probably carbon. The author suggests that, as Berthelot supposed, a lower oxide of carbon may have been formed. Gautier[84] has repeated Berthelot's work on this subject, and has failed to find any indication of a suboxide of carbon. When carbon monoxide, prepared by the method used by Berthelot, is heated strongly, no deposit of carbon is found, but since it contained moisture, the author suggests that, instead of forming free carbon, a hydrocarbon is produced.

A considerable amount of discussion has taken place with regard to the percarbonates, but it is considered that a summary of the points involved will be more useful if it is deferred until the experimental evidence is made more complete.

Silicon monosulphide has been obtained by Cambi[85] by heating ferrosilicon with sulphur in an electric arc furnace. The compound sublimes in two forms at 940° at reduced pressure, namely, a black solid and a yellow powder, the yellow modification being condensed on the cooler parts of the tube. Both forms, on analysis, appear to have the formula SiS. The black variety dissolves in water with the evolution of hydrogen sulphide and the formation of soluble silicic acid, whilst the yellow modification gives hydrogen sulphide and forms a white, insoluble substance which evolves hydrogen when treated with alkalis.

Group V.

The effect of radium emanation on ammonia has been investigated by Usher.[86] According to his results, ammonia is decomposed by the emanation at the ordinary temperature, and, what is rather surprising, the reverse action takes place only to a small extent. Similar results were obtained when solid ammonia at −190° was

[82] *Trans.*, 1910, **97**, 1226. [83] *Compt. rend.*, 1910, **150**, 1324; *A.*, ii, 707.
[84] *Ibid.*, 1383; *A.*, ii, 607.
[85] *Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 294; *A.*, ii, 952.
[86] *Trans.*, 1910, **97**, 400.

treated with solid emanation, although the action naturally was slow.

Some new metallic nitrides have been prepared by Fischer and Schröter [87] by forming an arc between silver as the anode and the metal concerned as the cathode, the electrodes being immersed in a liquid mixture of 90 per cent. of argon and 10 per cent. of nitrogen. The rapid cooling of the liquefied gas serves to prevent the decomposition of the newly-formed compounds. The elements sodium, potassium, rubidium, cadmium, iridium, thallium, lead, arsenic, antimony, and tellurium were shown to give nitrides. They were in most cases not pure, but contained particles of disintegrated metal. They are true nitrides, and not derivatives of azoimide. Gold, nickel, cobalt, and the platinum metals do not form nitrides under the experimental conditions described.

According to Raschig,[88] hydrazine can be readily obtained from hydrazine hydrate by treatment with solid sodium hydroxide. Equal quantities are heated together in a distilling flask very slowly to 150°. Anydrous hydrazine distils over as a strongly fuming liquid, which is quite stable.

The varieties of phosphorus have been a subject of much discussion during the last two years, the chief point of dispute being whether red phosphorus and Hittorf's phosphorus (obtained by crystallisation from melted lead) are separate entities. Cohen and Olie [89] have asserted that from experiments on the specific gravity, heats of combustion, fusion and vapour pressure of various samples of red phosphorus, only two varieties of phosphorus exist, namely, white phosphorus and Hittorf's so-called metallic phosphorus. They consider that red phosphorus is a solid solution of white phosphorus in the metallic variety. Stock [90] points out that if this were true, the proportion of white phosphorus, as deduced from the specific gravities, would be as high as 30 per cent., and this is not in accordance with its physical and chemical behaviour; he regards red phosphorus as a solid solution of several varieties of red phosphorus in each other, and agrees with Cohen and Olie's main conclusion that white phosphorus and Hittorf's phosphorus are the only two modifications of this element. The same author, with Gomolka,[91] has made a careful preparation of Hittorf's phosphorus, but finds, as all previous workers have found, that the purest product obtainable still contains 1·5 per cent. of lead. Jolibois,[92] on the other hand, maintains the view that red phosphorus is an

[87] *Ber.*, 1910, **43**, 1465; *A.*, ii, 605. [88] *Ibid.*, 1927; *A.*, ii, 706.
[89] *Chem. Weekblad*, 1909, **6**, 821; *A.*, 1909, ii, 998.
[90] *Chem. Zeit.*, 1910, **34**, 254; *A.*, ii, 288.
[91] *Ber.*, 1909, **42**, 4510; *A.*, ii, 30.
[92] *Compt. rend.*, 1910, **151**, 382; *A.*, ii, 846.

individual modification, but asserts the existence of a third variety, which he terms pyromorphic. This was obtained by heating red phosphorus[93] in a vacuum to 360°, when its density increases from 2·18 to 2·37. It must be pointed out, however, that such increases in density of substances by heating are not at all uncommon, and do not necessarily indicate the formation of a new entity. On reviewing all the evidence, the writer has come to the conclusion that the work of Chapman,[94] which showed that red phosphorus and Hittorf's phosphorus were identical, still stands. Many of the researches quoted above have been done with commercial red phosphorus, which, it should be noticed, always contains some yellow phosphorus. The writer is inclined to believe, from his own experiments, that carefully purified red phosphorus, when sealed up in a vacuum for a long time, undergoes a slow change to ordinary phosphorus, and that this change, slow as it is, may account for some of the discrepancies in the work of the authors who have investigated the subject.

A new chloride of phosphorus has been prepared by Besson and Fournier[95] by submitting a mixture of phosphorus trichloride and hydrogen to the action of the silent electric discharge. A yellow solid is formed at the same time. The liquid is fractionally distilled under diminished pressure, and after purification it is found to have the composition P_2Cl_4. It is easily oxidisable in air, taking fire spontaneously in certain circumstances. With water, phosphorous acid and a yellow solid are produced.

Perphosphoric acid has been studied by Schmidlin and Massini.[96] They show that electrolysis of phosphoric acid and its salts does not give rise to higher oxidation products, neither does phosphoric acid react with hydrogen peroxide. When, however, hydrogen peroxide (30 per cent.) is mixed with either metaphosphoric acid or with phosphoric oxide at low temperatures, a liquid is obtained which has strong oxidising properties. Manganese salts are even oxidised to permanganic acid by the liquid. The analysis points to the formula $PO(HO)_2 \cdot O \cdot OH$, so that the acid is tribasic. When pyrophosphoric acid in excess is treated with hydrogen peroxide, another perphosphoric acid, $H_4P_2O_8$, is obtained in small quantity.

Group VII.

The reaction of chlorine, dissolved in carbon tetrachloride, with a large number of metallic oxides has been investigated by Michael

93 *Compt. rend.*, 1909, **149**, 287; *A.*, 1909, ii, 726.
94 *Trans.*, 1899, **75**, 734.
95 *Compt. rend.*, 1910, **150**, 112; *A.*, ii, 1112.
96 *Ber.*, 1910, **43**, 1162; *A.*, ii, 498.

and Murphy.[97] At different temperatures most of the oxides react, producing chlorides. Ferrous oxide gives ferric oxide and ferric chloride even at −18°, whilst the similar reaction with cobaltous oxide only takes place at 100°. Silver oxide reacts at the ordinary temperature, giving silver chloride and carbonyl chloride; litharge gives lead dioxide and lead chloride at 100°. The oxides of molybdenum, tungsten, and uranium are the most resistant, requiring temperatures of 225—280° to complete the reaction.

Similar work has been done by Camboulives [98] with the vapour of carbon tetrachloride passed over the heated oxide at temperatures between 218° and 580°. In general, the results were the same as those of the American chemists. Boron trioxide and silica were unaltered by the treatment, but a difference, of which one can scarcely overestimate the importance as regards mineral analysis, was noticed between the behaviour of free and combined silica. The latter alone is attacked, and a method is available for readily distinguishing between these constituents of a mineral.

Group VI.

An important paper on the decomposition of ozone, by D. L. Chapman and H. E. Jones,[99] gives the results of heating ozone to 100° in presence of various other gases. It is shown that the presence of oxygen, nitrogen, carbon dioxide, carbon monoxide, and probably water vapour are without influence on the rate of decomposition. Nitrogen peroxide and chlorine very considerably accelerate the rate of decomposition. The influence of moisture was found to be practically nil. The experiments show that the change is a bimolecular one. M. Beger [1] has noticed that when ozone is decomposed at 350° a phosphorescent light is observable. This phosphorescence is much more marked if a hot glass rod be brought near the surface of liquid ozone. Remsen and Southworth [2] many years ago asserted that when ozone was decomposing in presence of carbon monoxide, no carbon dioxide was produced. Clausmann [3] maintains the contrary. He finds that the mixture of gases reacts strongly in sunlight, and slowly in the dark, the carbon dioxide formed producing a copious precipitate when passed through barium hydroxide solution.

A new synthesis of Caro's acid is given by D'Ans and Friederich.[4] Chlorosulphonic acid is treated with the calculated quantity of

[97] *Amer. Chem. J.*, 1910, **44**, 365; *A.*, ii, 1068.
[98] *Compt. rend.*, 1910, **150**, 175, 221; *A.*, ii, 202. [99] *Trans.*, 1910, **97**, 2463.
[1] *Zeitsch. Elektrochem*, 1910, **16**, 76; *A.*, ii, 287.
[2] *Ber.*, 1875, **8**, 1414; *Journ. Chem. Soc.*, 1876, i, 341.
[3] *Compt. rend.*, 1910, **150**, 1332; *A.*, ii, 608.
[4] *Ber.*, 1910, **43**, 1880; *A.*, ii, 706.

100 per cent. hydrogen peroxide in a freezing mixture. After removal of the hydrogen chloride in a vacuum, a crystalline mass is left, which melts about 45°, and is comparatively stable. If a second molecule of chlorosulphonic acid be added to the Caro's acid, persulphuric acid, $H_2S_2O_8$, is obtained in crystals. This acid is much more stable than Caro's acid, and can be kept for months.

Group VIII.

Fischer and Hähnel[5] have elaborated their apparatus for the preparation of argon from air. An iron tube containing calcium carbide serves to eliminate nitrogen and oxygen, and the carbon monoxide is burnt by copper oxide, and carbon dioxide absorbed by potassium hydroxide. The gas is caused to circulate by a mercury pump, and it was noticed that as the argon became more pure, the phosphorescence between the falling drops of mercury in the pump became brighter, until at the end of the preparation its light became visible in daylight. A similar effect was noticed by another worker as given by helium, and as it was shown by Collie[6] last year to take place to a very marked extent with neon, the phenomenon is supposed by the authors to be characteristic of the monatomic gases.

An easy method of obtaining argon is given by Claude.[7] The ordinary compressed oxygen of commerce is now very generally obtained from liquid air, and contains about 3 per cent. of argon. When the oxygen is removed by heated copper, there remains very little nitrogen to be eliminated by magnesium. The method will be of very great use to chemists who occasionally want a few cubic centimetres of a gas more inert than nitrogen.

The union of ferrous salts with nitric oxide[8] has been investigated by Manchot and Huttner. They found that the volume absorbed was diminished by the addition of small quantities of sulphuric acid, but was increased by increasing the concentration of the sulphuric acid up to 82 per cent. This solution and those having a still higher concentration of sulphuric acid are red in colour, and contain the compound $FeSO_4{\cdot}NO$. It crystallises in small, red leaflets. Similar results were obtained with a hydrochloric acid solution of ferrous chloride. The authors have drawn the conclusion that in no circumstances is more nitric oxide absorbed than corresponds with one molecule to one molecule of the ferrous salt.

H. B. BAKER.

[5] *Ber.*, 1910, **43**, 1435 ; *A.*, ii, 608.
[6] *Proc. Roy. Soc.*, 1909, **82**, A, 378 ; *A.*, 1909, ii, 663.
[7] *Compt. rend.*, 1910, **151**, 752 ; *A.*, ii, 1061.
[8] *Annalen*, 1910, **372**, 153 ; *A.*, ii, 414.

ORGANIC CHEMISTRY.

A STUDY of the investigations dealing with organic chemistry which have been published during the last few years produces a vivid impression of the perfection that has been attained by the doctrines of structural chemistry. The constitution of even the most complex compounds may be attacked with the confidence that the solution is dependent chiefly on experimental skill, and that unforeseen theoretical difficulties are unlikely to present themselves in the course of the investigation. A natural consequence of this state of things is that the majority of purely organic investigations proceed along more or less conventional lines, and their chief interest then lies either in the practical value of the results obtained, or in the employment of a new reagent, or of a new synthetical or analytical method possessing intrinsic interest. In other words, the structural organic chemistry of the present day is based on the application of certain well-established principles to complex cases. How perfect the adaptation of structural theory to experience has become is seen in stereochemistry, originally a daring extension of the conceptions of atomic linking which form the foundation of theoretical organic chemistry, but now an accepted doctrine, the conclusions of which are verified in the most complete manner by experience. It is this very perfection of the hypotheses employed that tends to diminish the novelty of the results attainable in the field of pure structural organic chemistry. To say this is not to depreciate the value of synthetical researches, or to deny the existence of many unsolved problems of very great interest, but such problems refer rather to difficult applications in special cases than to fundamental principles.

The opinion was expressed in last year's report that the recent development of organic chemistry has been largely determined by the influence of biology on the one hand, and of physics on the other. The same tendencies become more strongly marked every year. The problems connected with the chemistry of living matter are approached from two sides, the purely chemical and the physiological, and although the two lines still remain separated by a considerable interval, their gradual convergence is clearly discern-

able. From the chemical side, slow but steady advances are being made, both by analytical and synthetical methods, especially in the important department of protein chemistry. Amongst compounds, the constitution of which is unknown, and to which methods of determining structure have scarcely been applied, the enzymes are of primary importance. The study of their physico-chemical behaviour continues to make progress, but little advance has been made in the means of determining their homogeneity or of isolating definite chemical individuals in this class of substances. The question of the presence of minute quantities of certain metals as essential constituents, particularly of manganese in the oxydases, has a special interest in view of the known influence of traces of metals in bringing about syntheses at the ordinary temperature, such, for instance, as the effect of iron salts in Fenton's researches. The presence of iron as an essential component of hæmoglobin, and of magnesium in chlorophyll, gives some indication of the importance that this question, of the part played by metallic atoms in compounds capable of exercising a "catalytic" influence in physiological changes, is likely to attain. The manner in which such atoms are linked to the remainder of the molecule presents certain difficulties, referred to below, which have not yet received a satisfactory explanation. An allied field of research, the connexion between the physiological activity of compounds and their chemical constitution, attracts much attention, which, however, has not yet succeeded in dispelling the obscurity that surrounds it.

Turning to the side of organic chemistry most influenced by physics, we find that the energies of investigators are increasingly directed towards the elucidation of the relations between the physical properties of compounds and the structure of the molecules which compose them. Such researches have a twofold aim. On the one hand, it is sought to establish relations of this kind as a means of determining constitution in cases in which it is unknown, whilst, on the other, it is desired to represent the sum of the properties of any given substance as a consequence of the arrangement and linking of the atoms composing its molecule. It is the attention devoted to these aspects of organic chemistry that has compelled the renewed consideration of the validity of those conceptions which prove so satisfactory as long as only structural questions are involved. This is particularly noticeable in respect to the conception of valency. Whilst, from the purely synthetical point of view, the accepted valencies of the elements only rarely present any obstacle to the determination of structure (the quadrivalency of oxygen, the tervalency of iodine, etc., under certain conditions being accepted without question by almost all chemists),

the case is altered when the object sought is the explanation of physical properties or of chemical reactivity. The fact that an atom or group of atoms may influence the properties of an atom with which it is not immediately linked is not indicated by the conventional structural formulæ. The conception of "residual affinity," or of a capacity for addition possessed by a molecule or radicle after the ordinary valencies of the component atoms have been apparently satisfied, is playing a most important part in these more recent developments of the science. Thiele's views as to the distribution of affinity in unsaturated molecules have proved exceedingly fruitful, and the assumption that the attractive power of an atom is divisible to a greater extent than is implied by the valency assigned to it is more and more generally employed. The statement in last year's report (p. 57), that "the distribution of residual affinity in the molecule, with all that it implies, is the central problem of organic chemistry at the present time," may be repeated in view of the tendency apparent in the most recent work.

It must be admitted that the conception of partial valency is at present tentative and vague, and it is not possible to form a very distinct physical idea of the condition implied, but this defect is inevitable for a time, and need not hinder its application. The hypothesis is to be tested by its practical usefulness rather than by its consistency with any particular view as to the physical nature of chemical affinity.

Another aspect of the problem of valency is presented by the attempt to correlate chemical constitution, crystalline form, and physical properties by means of Pope and Barlow's doctrine of valency volumes, the extension of which to different classes of organic compounds is proceeding rapidly. This is a most interesting instance of a hypothesis on trial, and its possibilities of development appear to be considerable.

The study of a recent careful compilation of the relations between the physical properties and the chemical constitution of organic compounds [1] shows very clearly the limited extent to which such relations have been established, and the vast field that yet remains to be explored. Minor relations, valid only within the limits of a certain group of substances, abound, but important generalisations, worthy of being called laws, are conspicuously rare. In this connexion, it is of interest to observe that several important papers have appeared recently, in which the relations obtained by former workers, particularly in regard to refractivity and to the thermo-

[1] S. Smiles, *Relations between Chemical Constitution and Some Physical Properties*, London, 1910.

chemical constants, have been subjected to revision in the light of more recent data.

A department of chemistry which has received a remarkable amount of attention in recent years is that dealing with colloidal substances, and a glance through the pages of the important journal devoted entirely to this subject makes evident the fact that the most diverse branches of chemical investigation are being profoundly influenced by the study of colloids. This influence is either direct, as in the chemistry of vital products and of dyes and tanning materials, or indirect, as in the introduction of colloids, or mixtures of colloids, as "catalytic" agents for the purpose of bringing about or accelerating chemical reactions. The latter application is on the increase, and presents a special interest from the possibility thus afforded of bringing about chemical changes at the ordinary temperature and in the absence of acids, bases, or energetic condensing agents. In this way, by approaching more nearly to the conditions existing in the living organism, a partial bridging over of the gap between the synthetical processes of the laboratory and of the organism becomes possible.

As in previous years, it has been necessary to make a selection, for the purpose of this report, from the papers abstracted during the year, and the endeavour has been made to give special attention to investigations bearing on the general questions alluded to above. Amongst special problems, the knowledge of the terpenes has been added to in several important respects, and further advances have been made in the investigation of many alkaloids and other naturally occurring substances. Much of interest has also arisen from the study of organic compounds containing sulphur, the influence of this element in modifying the properties of organic compounds in which it occurs being sometimes very remarkable.

The Theory of Chemical Reactions.

Investigations having for their object the elucidation of the mechanism of reactions of carbon compounds continue to yield interesting and important results, but it cannot be said that any striking advances have been made during the year, and with one or two exceptions no theoretical suggestions of a novel or stimulating character have been made. Interest can no longer attach in any degree to sweeping generalisations in favour of purely ionic or purely non-ionic theories of any type of reaction in carbon compounds, although even now experienced workers in the subject are not always averse from making such one-sided pronouncements. In some cases, the evidence strongly supports an ionic explanation, and in others the reverse obtains, and all who have considered these

matters with an open mind are fully alive to the changes which may be rung on these possibilities. While the electrolytic dissociation hypothesis pictured the ions as chemically free atoms or groups, it offered an attractively simple explanation of many observations, but with the growing recognition that ions in solution are probably united chemically as well as electrically with the solvent, the simplicity has disappeared, and there is little except the influence of electrical charges to distinguish reactions of ions from those of other molecules. Much the same is true of the vexed question of intramolecular versus intermolecular migrations of atoms or groups; and until some entirely novel conception appears, there simply remains the test of experiment to decide between a variety of obvious alternatives in each special case.

In last year's report, reference was made to the work which is being done by Goldschmidt, Orton, Titherley, Auwers, and others in this department of organic chemistry, and their contributions during the year 1910 include much that will find a permanent place in the literature, although the results cannot again be dealt with in detail here. Other communications from the laboratories of the Johns Hopkins University [2] afford evidence that organised and strenuous efforts are being made to solve some of the outstanding problems connected with tautomerism and reaction mechanism in general, and important advances in the near future may confidently be anticipated. The most interesting theoretical communication is probably that which appears from the pen of one of the pioneers in this region, some of the fruits of whose experience and thought have been assimilated almost unconsciously by the younger school of organic chemists, and may almost be said to form part of their theoretical system. The appearance of the thesis entitled "An Outline of a Theory of Organic Chemistry founded on the Law of Entropy" [3] must therefore be regarded as an interesting event. This paper deserves careful study as representing the mature views which this ingenious worker has formed after many years of thought concentrated upon the nature of the reactions of organic compounds. Possibly it might prove dangerous to the peace of mind of a student imperfectly grounded in the principles of thermodynamics, for the familiar terms of the latter science are here put to unorthodox uses.

The author postulates the principle that a chemical system will always change in such a way that on the whole the greatest increase

[2] S. Nirdlinger and S. F. Acree, *Amer. Chem. J.*, 1910, **43**, 358; **44**, 219; S. Nirdlinger, E. K. Marshall, and S. F. Acree, *ibid.*, 358; E. E. Reid, *ibid.*, 489; R. F. Brunel and S. F. Acree, *ibid.*, 505; *A.*, i, 341, 785, 444, 481, 520.

[3] Michael, *J. Amer. Chem. Soc.*, 1910, **32**, 990; compare also, *ibid.*, p. 322, and *Ber.*, 1910, **43**, 621; *A.*, i, 285.

in entropy occurs unless such a consummation is opposed by some chemical hindrance. This principle cannot be disputed, and the difficulties only arise in its application, but from this communication it may be gathered that by careful classification of data the relative free chemical energies associated with the molecules of isomeric compounds may be roughly gauged, and certain broad generalisations then reveal themselves. As an aid to such estimations, the elements are, as usual, assumed to be endowed with positive or negative electrical characters of varying degrees of intensity, and the accurate attainment of an electrical balance between the atoms in the molecule is regarded as a factor in the internal "neutralisation" or low content of molecular free energy, and inversely; the results may then be used in predicting the changes likely to occur in new combinations of circumstances. It was to be expected, however, that the originator of a system of chemistry based on the second law of thermodynamics would justify remarks such as the following (which refers to the alkylation of ethyl acetoacetate): "as the heat of formation of the *C*- is greater than that of the *O*-methyl derivative, its formation represents the maximum entropy of the system."[4] If this does not represent a mere reversion to the doctrine of Thomsen and Berthelot, it may be surmised that the author, in the course of the thermochemical investigations which are in progress under his direction, has obtained a sufficiently large number of data to show that when isodynamic isomerides are compared, the individual which at equilibrium is present in smaller amount has the greater heat of combustion in all cases. If this be so, a most important step forward has been made, and it will be possible to extend very greatly the application of thermochemical data to theoretical organic chemistry; it is worthy of note that such a generalisation certainly appears to be foreshadowed by the recent investigations of Auwers and his pupils, which are referred to elsewhere (p. 69). Attention should be drawn to the fact that "chemical hindrance," in the sense used in the above thesis, is not synonymous with "steric hindrance." The former is imagined as a resistance to a given increase in entropy; the latter, which is less definite, has been used to include much that might be classified under the former heading, but is also frequently applied to express the fact that a small change in a system corresponds with the attainment of maximum entropy, in such cases as this effect is traceable to the influence of certain atoms or groups in the neighbourhood of the reactive portion of a molecule. Thus the difficulty in replacing the hydrogen atom in methane by chlorine is attributable to "chemical

[4] *Loc. cit.*, p. 1003.

hindrance"; the difficulty in converting dimethylmaleic anhydride into the acid is said to be due to "steric hindrance," and is rather the result of the instability of the acid caused by the methyl groups than a low velocity of hydration due to chemical hindrance. The low esterification velocities of certain *oo*-disubstituted benzoic acids appear to represent cases of chemical hindrance, although it is still an open question whether this hindrance is due to true steric influences. These questions have been dealt with at length by other chemists, and the subject must be studied from every point of view.[5]

The hypothesis advanced by Stieglitz in explanation of the Hofmann change of bromoamides and of the Beckmann change of oximes, assumed that at an intermediate stage there is formed a compound which contains a univalent nitrogen atom. Schroeter has recently adopted this view,[6] the details of his interpretation of that hypothesis in its application to oxime transformation being expressed by the following scheme:

$$R_1R_2C{:}NOH \xrightarrow{HCl} R_1R_2C{<}{}^{Cl}_{N{<}{}^{H}_{OH}} \longrightarrow R_1R_2C{<}{}^{Cl}_{N} \longrightarrow R_1C{<}{}^{Cl}_{NR_2}$$

This proposition, which was approved by Stieglitz,[7] has been subjected to effective criticism on the ground that it is not consistent with what is known of the behaviour of the isomeric pairs of oximes formed by unsymmetrical ketones. The hydrogen chloride additive products from one member of a pair would be identical with those from the other, and the same would therefore apply to the final transformation products; it is inferred that the central idea of Stieglitz's explanation is not tenable.[8]

Studies of the influence of experimental conditions on the mode of chlorination of toluene have yielded results which will doubtless prove of great value in subsequent discussions on the mechanism of substitution processes in aromatic compounds. On determining the proportion of side-chain substitution products to nuclear substitution products, it was found that access of light raised the proportion from 16 to 60 per cent. when concentrated aqueous hydrochloric acid was in contact with the toluene; if moist gas was passed into toluene alone, the proportion was about 60 per cent., rising to 90 per cent. in presence of light; with dry gas in the dark, the proportion was 90 per cent., in which case, naturally, light caused a relatively small rise in the ratio. The distribution of the chlorine in the products obtained in the dark was largely dependent on the amount of water present; in the complete absence of moisture, the proportion of benzyl chloride rose to 90 per cent., whilst 62 per cent. was

[5] Compare B. Flürscheim, *Trans.*, 1910, **97**, 84, and *Ann. Report*, 1909, 58.

[6] *Ber.*, 1909, **42**, 2336; *A.*, 1909, i, 617.

[7] *Ibid.*, 1910, **43**, 784; *A.*, i, 323. [8] P. J. Montagne, *ibid.*, 2014; *A.*, i, 623.

obtained when moist gases were used, and only 16 per cent. when all the materials were saturated with moisture; in all cases the chlorine used was obtained by electrolysing hydrochloric acid. Incidentally, it was observed that when moist chlorine is passed into boiling toluene in the light, the hydrocarbon gradually assumes a yellow colour, which it retains after washing; this colour is removed when hydrogen chloride is introduced in the light, reappearing when the supply of this gas is cut off.[9]

The velocity of hydration of acid anhydrides in aqueous solution has been determined by measuring the conductivity of the solution at intervals, and calculating the corresponding amounts of free acid, the necessary allowance for the variation of the properties of the medium being determined by subsidiary viscosity measurements. The reaction is nearly of the unimolecular type when small concentrations of anhydride were employed, and the results obtained indicate that the reaction is not accelerated by the presence of hydrogen ions. No reference is made to the well-known effect of small quantities of sulphuric and other powerful acids in accelerating acetylation of water, hydroxy-compounds, and weak bases, with acetic anhydride.[10]

It appears probable that acetylation by anhydrides, like esterification by the free acids, may proceed by either or both of two paths, one which is brought about or accelerated by the agency of a "catalyst," and the other which may be termed automatic; the former would probably be more evident in indifferent non-aqueous media.

The interaction between silver nitrate and α-halogen derivatives of fatty acids (or their sodium salts) is much accelerated by the presence of small quantities of silver bromide or iodide; silver iodide also exerts a similar influence on the speed of the reaction between silver nitrate and methyl iodide, and this effect is probably connected with the tendency of the silver halogen salts to persist in a colloidal condition. The most satisfactory explanation of the quantitative results obtained in this investigation is that the main reaction between the halogen-substituted acids and silver salts is one taking place between the $Ag^{\cdot}$ ions and the anions of the organic acid, which is consistent with the view that the electrical attractions or repulsions between ions with opposite or like changes may greatly influence reaction velocities.[11]

In this communication, attention is also drawn to a retarding influence exerted in the case of halogen-substituted acids by the nitric acid formed, an effect also produced by the addition of

[9] J. B. Cohen, H. M. Dawson, J. R. Blockey, and A. Woodmansey, *Trans.*, 1910, 97, 1623.
[10] A. C. D. Rivett and N. V. Sidgwick, *ibid.*, 732, 1667.
[11] G. Senter, *ibid.*, 346; compare *Ann. Report*, 1909, 70.

benzenesulphonic acid or, to a much smaller extent, lactic acid; thus the reactions between silver salts and organic halogen compounds are complicated by a variety of disturbing side effects, as was indicated by the previous work of Burke and Donnan and other investigators. In continuation of researches on the reaction between silver salts and alkyl haloids, it was observed that using as solvent the filtered liquid from a previous experiment, free from silver salt or alkyl iodide, the change proceeded more rapidly than with the original solvent, and to an extent which accounted for the abnormalities noted in the earlier experiments of Burke and Donnan; a number of interesting observations are also recorded, some of which cannot yet be satisfactorily explained.[12]

The so-called catalytic influence of acids and bases on numerous reactions has been generally associated with their affinity constants, and discrepancies in the expected order of their activities have frequently been traced to a variation of their affinity coefficients with the nature of the medium in which they may be dissolved. Since Knoevenagel's discovery that in certain cases tertiary bases, however powerful, are relatively inefficient as "catalysts," it became evident that some specific action occurs in many cases, and the influence of primary and secondary bases has been explained by arguing that these form additive products in this manner, which

$$X + NHR_1R_2 = X{<}^{NR_1R_2}_{H}$$

is impossible in the case of tertiary bases, and these additive products are assumed to be much more reactive than the original compound, although in many cases no very obvious reason for this appears.

Reactions similar to those brought about by bases such as piperidine are also observed with certain amino-acids, peptones, proteoses, or even proteins; thus, for instance, furfuraldehyde does not condense with malonic acid, but does so in presence of glycine or alanine. The observation suggests that such nitrogenous compounds may be effective as "catalysts" in certain processes occurring in the living cell.[13]

Most interesting evidence corroborating the view that bases may exert a specific "catalytic" influence has been obtained with the aid of optically active compounds. Bases greatly accelerate the decomposition of camphorcarboxylic acid by heat into carbon dioxide and camphor, and it is now found that the *l*-camphorcarboxylic acid decomposes 46 per cent. faster than the *d*-acid in presence of quinine, and the *d*-acid 46 per cent. faster than the *l*-acid in presence of quinidine; consequently, when inactive camphor-

[12] F. G. Donnan and H. E. Potts, *Trans.*, 1910, **97**, 1882.
[13] H. D. Dakin, *J. Biol. Chem.*, 1909, **7**, 49; *A.*, i, 101.

carboxylic acid is partly decomposed in presence of quinine, the camphor formed is slightly lævorotatory, and the remaining acid slightly dextrorotatory. The results obviously have an important bearing on the question of the mechanism of the specific actions of enzymes and of asymmetric synthesis by "catalytic" action.[14]

An interesting photo-chemical reaction is the conversion, in indifferent solvents, of *o*-nitrobenzaldehyde into *o*-nitrosobenzoic acid, whilst in alcoholic solution an ester of this acid is produced. The latter reaction is remarkable, as the acid is not esterified if dissolved in an alcohol and exposed to light. The chance observation that *o*-nitrobenzaldehydediethylacetal is converted into ethyl *o*-nitrosobenzoate by light gave the explanation of the reaction, which evidently takes place in the following stages:

$$NO_2\cdot C_6H_4\cdot CHO \longrightarrow NO\cdot C_6H_4\cdot CH(OEt)_2 \longrightarrow$$
$$[NO\cdot C_6H_4\cdot C(OEt)_2\cdot OH] \longrightarrow NO\cdot C_6H_4\cdot CO_2Et + Et\cdot OH.$$ [15]

The results of experiments with compounds containing various substituents, and with different alcohols, are considered to favour Henry's view of the esterification of an acid, namely, that the mono-alkylated ortho-acid appears as an intermediate product, thus:

$$\cdot C\Big\langle{}^{O}_{OH} \xrightarrow{R\cdot OH} \cdot C\!\begin{array}{l}\diagup OR\\ -OH\\ \diagdown OH\end{array} \longrightarrow \cdot C\Big\langle{}^{OR}_{O} + H_2O$$

and a similar scheme is proposed for the etherification of phenols.

The chemistry of phototropic changes remains, however, very obscure. The examination and comparison of a large number of hydrazones and osazones has failed to reveal any relation between constitution and liability to undergo phototropic change, especially amongst the osazones, although a few minor regularities have been detected in other groups.[17] Again, whilst light usually brings about the conversion of labile ethylene derivatives into their stable stereoisomerides, the reverse change into the labile modification under the influence of ultra-violet light occurs in the coumaric acid series.[18]

The Influence of Unsaturation.

A great variety of work might be grouped under this heading, numerous investigations having dealt with the effect produced on either the physical or the chemical properties of compounds by the state of unsaturation of the molecule. The first place may be given to the influence on certain physical properties, namely,

[14] K. Fajans, *Zeitsch. physikal. Chem.*, 1910, **73**, 25; *A.*, ii, 599.
[15] E. Bamberger and F. Elger, *Annalen*, 1910, **371**, 319; *A.*, i, 267.
[17] F. Graziani, *Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 190; M. Padoa and F. Graziani, *ibid.*, 193; M. Padoa and L. Santi, *ibid.*, 302; *A.*, i, 777, 778, 779.
[18] R. Stoermer, *Ber.*, 1909, **42**, 4865; *A.*, i, 114.

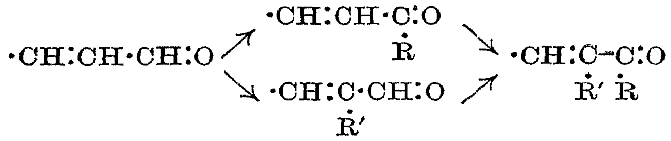
refractivity and dispersive power, heat of combustion, and magnetic susceptibility. Short accounts of some chemical methods of studying unsaturation, and of some of its effects on reactivity then follow, whilst other matter relating to unsaturation is to be found in the section on colour and constitution, and elsewhere.

Physical Properties.—The refractivity of an organic compound is intimately related to the number and arrangement of the double linkings in the molecule, and measurements of refractivity have therefore rendered most important services in the determination of constitution, especially in the terpene series. In such cases, the relations employed are those originally found by Brühl. Apparent exceptions have been observed from time to time, and an extended investigation has now been undertaken,[19] with the object of removing such anomalies. It is found that the existence of optical exaltation due to unsaturation is best determined by comparing specific, and not molecular, refractivities and dispersive powers. Under these conditions, a few apparent anomalies, due merely to the multiplication of small errors, disappear.

Only two classes of compounds have been observed to exhibit marked optical exaltation without the presence of conjugated double linkings. These are the methene derivatives, $>{:}C<$, containing a semicyclic ethylene linking, and compounds containing a ring of three carbon atoms, the conjugation of the latter system with a double linking giving a remarkably great exaltation. A number of instances in which an expected exaltation does not occur are explained by the disturbing influence of side-chains attached to the central carbon atoms of a conjugated system. Thus the exaltation diminishes in the series:

$$\cdot CH{:}CH\cdot CH{:}CH\cdot \longrightarrow \cdot CH{:}\underset{\dot{R}}{C}\cdot CH{:}CH\cdot \longrightarrow \cdot CH{:}\underset{\dot{R}}{C}\cdot\underset{\dot{R}}{C}{:}CH\cdot$$

or in the series:



the chemical nature of the substituent having an influence on the amount of the depression. If further substitution takes place, so that side-chains are attached to the terminal as well as to the central atoms of such a system, the exaltation is further diminished, prac-

[19] K. Auwers and F. Eisenlohr, *Ber.*, 1910, **43**, 806, 827; *J. pr. Chem.*, 1910, [ii], **82**, 65; *A.*, ii, 365, 367.

tically vanishing in such systems as $\cdot\underset{R}{C}{=}\underset{R'}{C}{-}\underset{R''}{C}{:}O$ and $\cdot\underset{R}{C}{=}\underset{R'}{C}{-}\underset{R''}{C}{=}\underset{R'''}{C}$. Systems containing Thiele's "crossed double linkings" show exaltation, but in a less degree than in normal chains. Repeated conjugation in a straight chain gives very high exaltation. The formation of a ring has the same effect as the introduction of side-chains; thus the systems $\begin{matrix}-C\\-C\end{matrix}\!\!>C\cdot\underset{R}{C}{:}CH$ and $\begin{matrix}-C\\-C\end{matrix}\!\!>C\cdot\underset{R}{C}{:}O$ resemble $\cdot CH{:}\underset{Me}{C}{-}\underset{R}{C}{:}CH$ and $\cdot CH{:}\underset{Me}{C}{-}\underset{R}{C}{:}O$ respectively.

The dispersive power is a more sensitive test for conjugation than the refractivity, often showing a distinct exaltation when nothing of the kind is observable in the latter property.

By comparing together a number of pairs of compounds, the second member of which differs from the first by the substitution of CH_2 for CO, such as:

Formaldehyde,	$CH_2{:}CO$	Acetone,	$CMe_2{:}CO$
Ethylene,	$CH_2{:}CH_2$	*iso*Butylene,	$CMe_2{:}CH_2$,

it is found[20] that the increase of refractivity thereby produced is practically constant, provided that only terminal groups are thus interchanged. Much greater differences are observed when the substitution of a ketonic for an ethenoid linking occurs in the middle of a chain, as in the pair:

Stilbene,	$Ph\cdot CH{:}CH\cdot Ph$
Benzophenone,	$Ph\cdot\underset{O}{\overset{}{C}}\cdot Ph$.

Auwers and Eisenlohr's conclusion, based on a very small number of observations, that alkyloxy-groups reduce the exaltation more than either alkyl or hydroxy-groups, is disputed on the ground of a comparison of the refractivities of a number of aldehydes with the corresponding methyl ketones, the differences being practically the same for unsaturated as for saturated compounds. A further application of the method is made to determine the constitution of several β-diketones, the results obtained being consistent with the other known properties of these compounds.

The change in constitution which accompanies the formation of salts from a pseudo-acid may also be followed by means of the change of refractivity.[21] A considerable exaltation is observed

[20] Miss I. Smedley, *Trans.*, 1910, **97**, 1475, 1484.

[21] A. Hantzsch and K. Meisenburg, *Ber.*, 1910, **43**, 95 ; *A.*, ii, 169.

during salt-formation, even when the original substance is truly enolic, thus suggesting that subsidiary valencies are concerned in the production of *aci*-salts (see p. 80). The change does not run entirely parallel with that of colour; thus, it is greater on passing from *p*-nitrophenols to their salts than in the more highly coloured ortho-series. The exaltation on forming a salt of such a substance as ethyl acetoacetate is greater than when alkyl or acyl derivatives are formed.

The effect of unsaturation on the heat of combustion has also been studied and brought into relation with the optical properties.[22] Many of the data existing in the literature are not comparable, owing to the comparative roughness of the thermochemical methods employed, but the improved forms of calorimetric bombs admit of an accuracy of 0·05 per cent., and results thus obtained have a high value in the determination of constitution. The more labile of a pair of isomerides has the higher heat of combustion. Hydrocarbons with conjugated double linkings always have a lower heat of combustion than their non-conjugated isomerides, and are thus to be regarded as more saturated, whilst the addition of side-chains to a conjugated system diminishes the effect. Generally, the thermochemical method is less convenient in its application than the optical, but it occasionally furnishes evidence of conjugation when optical methods fail, as in the case of phellandrene. It fails, however, with bicyclic terpenes.

The magnetic susceptibility of an organic compound may also be separated into two parts, one of which represents the sum of the atomic susceptibilities, whilst the other depends on the distribution of atomic linkings in the molecule.[23] Values of the latter have been determined for a number of different types of linking, and the method has been applied to the determination of structure. Azo-compounds and hydrazones, for example, give widely different values for the susceptibility, and a further means is thus provided of distinguishing between the two alternative structures. The colourless modifications of *p*-azoanisole and *p*-azophenetole, examined in this way, behave like azo-compounds, whilst the coloured modifications obtained from them by the action of heat give values corresponding with the hydrazone formula.

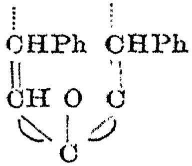
Chemical Properties.—A re-examination of Thiele's work on conjugated linkings has been undertaken by Borsche,[24] and the attempt has been made to determine, with greater precision, the distribution

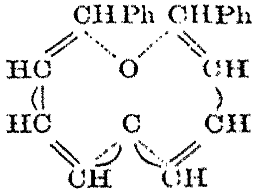
[22] K. Auwers and W. A. Roth, *Ber.*, 1910, **43**, 1063; *Annalen*, 1910, **373**, 239; K. Auwers, W. A. Roth, and F. Eisenlohr, *ibid.*, 267; *A.*, ii, 485, 585, 586.

[23] P. Pascal, *Compt. rend.*, 1910, **150**, 1167; *A.*, ii, 580.

[24] W. Borsche, *Annalen*, 1910, **375**, 145; *A.*, i, 680.

of residual affinity in molecules containing conjugated and crossed double linkings. The paper is too long to analyse at all fully, and the conclusions do not in any way invalidate the brilliant work of Thiele, but the latter is supplemented in several respects. The experimental part of the research consists chiefly of reactions between ethyl acetoacetate and compounds containing the system of crossed double linkings, $\underset{\substack{\vdots\\ \mathrm{O}}}{\mathrm{C{:}C{\cdot}C{\cdot}C{:}O}}$ If the chain of atoms is sufficiently long, the ends may approach one another so closely that a part of the residual affinity is saturated, and in accordance with this supposition it is found that ethyl acetoacetate combines with distyryl ketone (I), but not with dicinnamylideneacetone (II):


(I.)


(II.)

Unsaturated open-chain acids having a double linking in the $\alpha\beta$-position are conjugated, whilst their $\beta\gamma$- and other isomerides are not conjugated. The latter therefore show the more unsaturated character, and it is found [25] that the addition of bromine to them occurs so much more rapidly than in the former case that the difference of velocity may be employed as a method of distinguishing between the isomerides. Auwers also finds that the heat of combustion of $\alpha\beta$-unsaturated acids is less than that of acids in which the double linking is in the $\beta\gamma$-position.

The researches which have been carried out during the last five years by Harries and others, dealing with the action of ozone on unsaturated compounds, have been summarised recently,[26] with the addition of some further material. The reaction is a valuable one for the recognition of unsaturated groups, and for distinguishing conjugated from unconjugated double linkings, but in certain instances its indications are ambiguous. The ozone reaction with benzene derivatives, for example, has not been generally accepted as proving the existence of ethylene linkings in benzene. Such linkings are indicated as absent from the methylated benzenes when the test of oxidation by air in presence of powdered sodium hydroxide is applied, although this test is usually capable of detecting double linkings.[27]

[25] J. J. Sudborough and J. Thomas, *Trans.*, 1910, **97**, 715.

[26] C. D. Harries, *Annalen*, 1910, **374**, 288 ; *A.*, i, 607.

[27] K. W. Charitschkoff, *J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1152 ; *A.*, i, 104.

The addition of hydroxylamine to unsaturated compounds takes place only when the ethylene linking is suitably conjugated, and may be almost entirely prevented by the introduction of certain groups.[28] Thus, in the series:

Sorbic acid, $CHMe{:}CH\cdot CH{:}CH\cdot CO_2H$.

Piperic acid, $CH_2{<}^{O}_{O}{>}C_6H_3\cdot CH{:}CH\cdot CH{:}CH\cdot CO_2H$.

a-Phenylcinnamenylacrylic acid, $CHPh{:}CH\cdot CH{:}CPh\cdot CO_2H$.

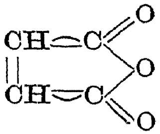
the first takes up hydroxylamine in the cold, the second and third only slowly on heating.

Grignard's reagent also finds frequent application in the study of unsaturated linkings. Compounds containing the chain $C{:}C\cdot C{:}O$, such as phenyl styryl ketone, give only saturated compounds with Grignard's reagent, but react with zinc or magnesium and methyl bromoacetate to form unsaturated compounds, such as methyl β-hydroxy-$\beta\delta$-diphenyl-Δ^{γ}-pentenoate,

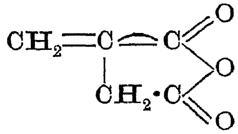
$$CHPh{:}CH\cdot CPh(OH)\cdot CH_2\cdot CO_2Me,$$

by addition in the $\alpha\beta$-position.[29]

Reactivity.—A series of measurements of the rate of hydration of acid anhydrides brings out incidentally the effect of conjugated double linkings on the velocity. Thus, whilst the constants for acetic and succinic anhydrides are practically the same, that for maleic anhydride (I) is ten times as great, whilst itaconic anhydride (II) exhibits only a slight increase[30]:



(I.)



(II.)

The system $C{:}C{:}C$, in which the double linkings are adjacent, possesses very high residual affinity, and allene compounds are correspondingly difficult to prepare. It might be expected that the system $C{:}C\cdot C{:}C{:}C$ would be intermediate in stability between an allene derivative and a conjugated compound. As an aromatic nucleus or a carbonyl group, attached to $\cdot C{:}C\cdot$, has the same effect as another ethylene linking, it might be expected that a compound $^{X}_{Y}{>}C{:}C{:}C{<}^{W}_{Z}$ would be stable if X, Y, W, and Z were all

[28] T. Posner and K. Rohde, *Ber.*, 1910, **43**, 2665; *A.*, i, 847

[29] E. P. Kohler and G. L. Heritage, *Amer. Chem. J.*, 1910, **43**, 475; E. P. Kohler and M. C. Burnley, *ibid.*, 412; *A.*, i, 484, 891.

[30] A. C. D. Rivett and N. V. Sidgwick, *Trans.*, 1910, **97**, 1677.

aromatic residues or carboxyl groups.[31] An attempt to prepare $\begin{matrix}C_{10}H_7\\C_6H_5\end{matrix}>C:C:C<\begin{matrix}C_6H_5\\CO_2H\end{matrix}$ led to an indecisive result, but the compound is probably stable, as is tetraphenylallene.

Another test of the reactivity of unsaturated compounds of the type $X\cdot CH_2\cdot R$, in which X is a halogen atom, is afforded by experiments in which these compounds are brought into contact with pyridine in alcoholic solution. The reactivity of X is then conditioned by the residual affinity of R, in the manner described in last year's report (p. 59). When the residual affinity is reduced by conjugation, the reactivity is also reduced. Thus, cinnamyl bromide, $Ph\cdot CH:CH\cdot CH_2Br$, in which the double linking is conjugated with a phenyl group, has less than one-half the reactivity of allyl bromide, $CH_2:CH\cdot CH_2Br$. In agreement with the results obtained by other methods, the residual affinity of the carbonyl group in ketones is found to be greater than that of carboxyl, indicating some affinity between the two oxygen atoms of the carboxyl group. In a phenyl ester, the phenyl absorbs much of the residual affinity of the hydroxylic oxygen, and the second oxygen atom thereby becomes more ketonic, so that the reactivity of the bromine atom in phenyl bromoacetate, $CH_2Br\cdot C<\begin{matrix}O\\OPh\end{matrix}$, is again increased.[32]

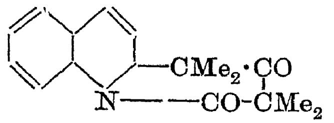
Keten Compounds.—As an appendix to the subject of unsaturation, some notes may be collected, dealing with two classes of compounds which derive their chief interest from their connexion with this subject, namely, the derivatives of keten and of triphenylmethyl.

Keten is conveniently prepared, when required as a reagent, by passing acetone vapour through a tube packed with fireclay at 500—600°: $CH_3\cdot CO\cdot CH_3 = CH_2:CO + CH_4$.[33] Combination with hydrogen cyanide takes place to form a compound, $C_5H_5O_2N$, which boils at 173°, but nevertheless reacts as if it were a mere mixture of its components. The formula $CH_2:C(OAc)\cdot CN$ is proposed tentatively.[34] It is now agreed[35] that the so-called acetylketen is *cyclo*butan-1 : 3-dione.

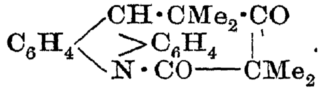
The formation of bases from dimethylketen by tertiary bases has also received further study, combination being found to take place through the C:N– linking. The formula (I) is now proposed for

[31] A. Lapworth and E. Wechsler, *Trans.*, 1910, **97**, 38.
[32] H. T. Clarke, *ibid.*, 416.
[33] J. Schmidlin and M. Bergmann, *Ber.*, 1910, **43**, 2821 ; *A.*, i, 816.
[34] Miss S. Deakin and N. T. M. Wilsmore, *Trans.*, 1910, **97**, 1968.
[35] Miss F. Chick and N. T. M. Wilsmore, *ibid.*, 1978.

dimethylketenquinoline, and the formula (II) for the compound with acridine [36]:



(I.)



(II.)

Compounds of the Triphenylmethyl Group.—Several additions have been made to our knowledge of this interesting group of compounds. An analogue of triphenylmethyl has been found, which exists in solution entirely in the unimolecular condition. This is tridiphenylmethyl, $(C_6H_5{\cdot}C_6H_4)_3C{\cdot}$, which forms deep violet solutions, green in thin layers. The solutions of its haloid compounds in liquid sulphur dioxide are coloured and conducting, and a white peroxide is very readily formed.[37] The authors retain for the present Gomberg's original formula, R_3C, rather than any of the modifications proposed.

In contrast with this compound, one in which the diphenylene residue takes the place of two diphenyl groups exists only in the bimolecular form, $C_6H_5{\cdot}C_6H_4{\cdot}\underset{C_6H_4{\cdot}C_6H_4}{C}$——$\underset{C_6H_4{\cdot}C_6H_4}{C}{\cdot}C_6H_4{\cdot}C_6H_5$, which is colourless, and yields only colourless haloid compounds.[38]

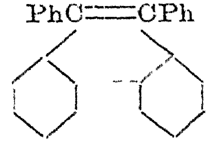
A third compound, $\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!>\!CPh{\cdot}CPh\!<\!\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}$, forms colourless solutions in benzene, which become coloured on heating, losing their colour again when cooled, so that dissociation may be suspected.[39] When diphenyl takes the place of phenyl, there is no change of colour on heating. Triphenyltrimethylethane, $CPh_3{\cdot}CMe_3$, behaves as a perfectly saturated hydrocarbon.

The connexion between the appearance of colour and of electrolytic conductivity in solutions of the haloid compounds of this class is less close than was supposed, as triphenylmethyl bromide dissolves in acetone, acetonitrile, and pyridine, and the solutions are colourless, and nevertheless conduct electrolytically. The conductivity of solutions in the last-named solvent gradually falls, owing to the formation of triphenylmethylpyridinium bromide.[40]

Tetraphenylethylene, $CPh_2{:}CPh_2$, behaves somewhat anomalously, being able to take up chlorine, but not bromine or iodine. The

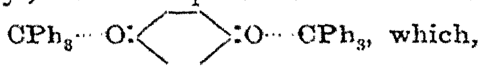
[36] H. Staudinger, H. W. Klever, and P. Kober, *Annalen*, 1910, **374**, 1; *A.*, i, 586.
[37] W. Schlenk, T. Weickel, and A. Herzenstein, *ibid.*, **372**, 1; *A.*, i, 236.
[38] W. Schlenk and A. Herzenstein, *ibid.*, 21; *A.*, i, 237.
[39] W. Schlenk, A. Herzenstein, and T. Weickel, *Ber.*, 1910, **43**, 1753; *A.*, i, 469.
[40] A. Hantzsch and K. H. Meyer, *ibid.*, 336; *A.*, i, 238.

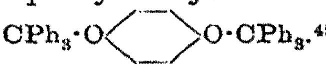
dichloride, treated with benzene and aluminium chloride, does not yield a further phenylated derivative, but undergoes a remarkable condensation to 9 : 10-diphenylphenanthrene:


.[41]

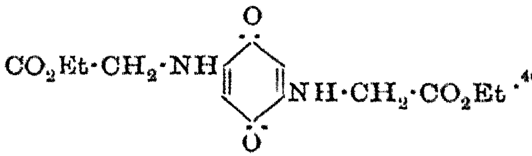
Diphenylene-ethylene, $\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}\!>\!C{:}C\!<\!\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}$, another member of this remarkable series of hydrocarbons, has a deep red colour.[42]

Colour and Constitution.

Last year's report (p. 64) referred to the attention given to coloured compounds of the quinhydrone class. The number of highly coloured additive compounds has again been very largely increased. In addition to the familiar quinhydrones, or additive compounds of quinones and dihydric phenols, many quinones combine with other phenols, yielding darker coloured products. On the other hand, aliphatic ketones, even if coloured, do not yield darker products with phenols.[43] The oxygen of the quinone is not essential, as quinone-chloroimide and -dichloroimide, $O{:}C_6H_4{:}NCl$ and $ClN{:}C_6H_4{:}NCl$, form exactly similar quinhydrones with quinol.[44] When *p*-benzoquinone is brought into contact with triphenylmethyl, the first product is an unstable, orange additive compound, , which, however, soon passes into the very stable triphenylmethyl ether of quinol,


.[45]

The reaction of *p*-benzoquinone with esters of amino-acids, resulting in the formation of highly coloured compounds, is less simple, hydrogen being eliminated from the amino-group, so that some quinol is formed. The product from glycine has the formula:


.[46]

[41] J. Schmidlin and R. von Escher, *Ber.*, 1910, **43**, 1153; *A.*, i, 369; H. Finkelstein, *ibid.*, 1533; *A.*, i, 469.

[42] J. Schmidt and H. Wagner, *ibid.*, 1796; *A.*, i, 550.

[43] K. H. Meyer, *ibid.*, 157; *A.*, i, 179.

[44] A. Knorr, *ibid.*, 798; *A.*, i, 324

[45] J. Schmidlin, J. Wohl, and H. Thommen, *ibid.*, 1298; *A.*, i, 377.

[46] E. Fischer and H. Schrader, *ibid.*, 525; *A.*, i, 270.

The great additive power of polynitro-compounds, such as tetranitromethane, was remarked last year, and has received further attention. *s*-Trinitrobenzene forms coloured additive compounds with arylamines, phenols, and phenol ethers, but not with aminophenols. Almost complete dissociation takes place in benzene solution, as is shown by determinations of the molecular weight.[47] *s*-Trinitrobenzene also forms coloured compounds with hydrazine, phenylhydrazine, and azobenzene. The colour thus produced is much deeper than when salts are formed, as in the hydrazine salts of nitrophenols. Trinitrotoluene only yields a very unstable red compound, and trinitroxylene and trinitromesitylene do not form coloured additive products.[48]

The relation between colour and constitution has been studied in a series of unsaturated ketones and salts derived from them.[49] The starting point of the research was the two compounds, distyryl ketone (I) and dibenzylidene*cyclo*pentanone (II):

$$\text{(I.)}\quad \begin{array}{ccccc} C_6H_5-CH=CH & - & C & - & CH=CH-C_6H_5. \\ & & \| & & \\ & & O & & \end{array}$$

$$\text{(II.)}\quad \begin{array}{ccccccc} & CH_2 & - & - & - & CH_2 & \\ & | & & & & | & \\ C_6H_5-CH= & C & - & C & - & C & =CH-C_6H_5. \\ & & & \| & & & \\ & & & O & & & \end{array}$$

The chromophoric groups in (I) are further reinforced by the formation of the ring, so that derivatives of (II) have a deeper colour than those of (I). By replacing the hydrogen of the phenyl residues by alkyl or alkyloxy-groups, the basicity of the ketone could be varied, and the colour of the solutions obtained on dissolving the substituted ketones in various acids compared. The more basic the ketone employed and the stronger the acid used as solvent, that is, the more complete the salt-formation, the deeper is the colour of the solution. By cooling to a low temperature in contact with hydrogen chloride, several molecules of the latter may be taken up, with corresponding intensification of the colour.

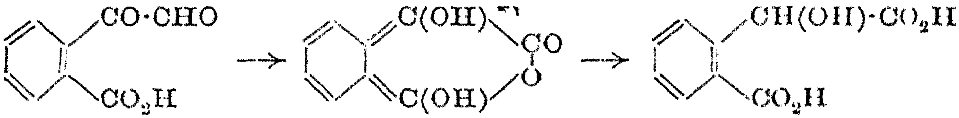
The quantitative effect of closing the ring on the colour of the derivatives examined and of their salts is always the same. If the chain of conjugated double linkings is increased by changing from benzylidene to cinnamylidene compounds, the colour is still further deepened, that is, the absorption is moved further towards the red. Furyl has a greater effect on the colour than phenyl. Precisely similar observations have been made with derivatives of fluorenone, and of chrysene and indene.

[47] J. J. Sudborough and S. H. Beard, *Trans.*, 1910, **97**, 773.
[48] K. A. Hofmann and H. Kirmreuther, *Ber.*, 1910, **43**, 1764 ; *A.*, i, 548.
[49] H. Stobbe, *Annalen*, 1909, **370**, 93 ; *A.*, 1910, i, 43.

Another interesting study relates to the aminocoumarins, which are coloured, and the colour is not destroyed when the amino-group is fully methylated, or when the two hydrogen atoms of the coumarin are replaced by methyl. Acylation, or the formation of a quaternary salt, destroys the colour. The hypothesis of an oscillation of linkings is proposed in explanation, on lines similar to those already suggested by other workers.[50]

Triketohydrindene hydrate is colourless, and must have the constitution $C_6H_4{<}{}^{CO}_{CO}{>}C(OH)_2$. Similar colourless additive compounds are obtained in which the water is replaced by guanidine or benzamidine.

Potassium hydroxide produces a solution which is first yellow, then blue, and then colourless, a series of changes which may be explained by the opening and closing of the ring in the following manner[51]:



Phenylglyoxal-*o*-carboxylic acid. → *o*-Quinonoid blue salt. → *o*-Carboxymandelic acid.

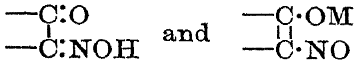
Incidentally, many other discussions of the relation between colour and constitution are found in communications dealing primarily with questions of structure alone.

Coloured Salts.—Reference has been made on several previous occasions[52] to the investigations of Hantzsch and others, dealing with compounds which form two or more series of differently coloured salts. Such cases of "pantochromism" are frequently puzzling, owing to the difficulty of distinguishing between true chemical isomerides and merely polymorphic modifications. It seems probable, in fact, that many instances of this kind lie just on the border-line, where a satisfactory formulation is at present beyond our powers, and the suggested explanations, sometimes stereochemical and sometimes resting on the principle of subsidiary valency, can only be regarded as extremely hypothetical, fulfilling the temporary purpose of classifying the phenomena.

One of the most familiar instances of pantochromism is that of violuric acid and its salts. The following are the principal conclusions arrived at from a study of these and other oximinoketone derivatives.[53] The colour of solutions of the violurates deepens from yellow and orange through red and violet to blue with increasing

[50] A. Clayton, *Trans.*, 1910, **97**, 1350.
[51] S. Ruhemann, *ibid.*, 2025. [52] *Ann. Report*, 1909, 67.
[53] A. Hantzsch, *Ber.*, 1910, **43**, 82; *A.*, i, 200.

positivity of the metal and increasing residual affinity of the solvent. All the solutions contain unimolecular salts. Spectroscopic examination shows that the pale yellow solutions of the ketones contain true oximino-compounds, whilst the blue solutions resemble nitroso-compounds. These differences may therefore be attributed to chemical isomerism:



Yellow. Blue.

The intermediate colours are due to mixture of these two forms, and may be imitated by mixing the pure modifications. Such facts as these do not, however, account satisfactorily for the simultaneous separation of both red and yellow crystals of the same salt from a single solution, or for the formation of a red and a yellow lithium salt, but of a blue and a flesh-coloured cæsium salt.

The oximino-oxazolones form unimolecular salts, those with weak bases being generally yellow, whilst those with strong bases are more or less blue, so that there is little difficulty in attributing the difference in colour to the predominance of the oximino-ketone form in the first, and of the nitroso-enol form in the second case.[54]

Similar relations are observed among the dimethyl- and diphenylviolurates.[55] These salts, however, undoubtedly form coloured additive compounds with certain solvents, such as pyridine and phenol, and such results point to the necessity of making full analyses before considering salts of this class as exhibiting true isomerism. In the case of the hydroxyazo-compounds, however, although the yellow series of salts generally separates with solvent of crystallisation, this does not appear to be the cause of the colour, but only to increase the stability of the yellow modification in the solid state, as each form yields solutions of its own colour.[56]

The formulæ proposed are:

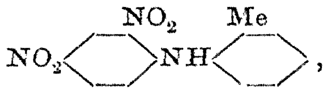
Yellow. Red.

which do not differ in any clear manner from those of a hydroxyazo-compound and a quinonehydrazone respectively.

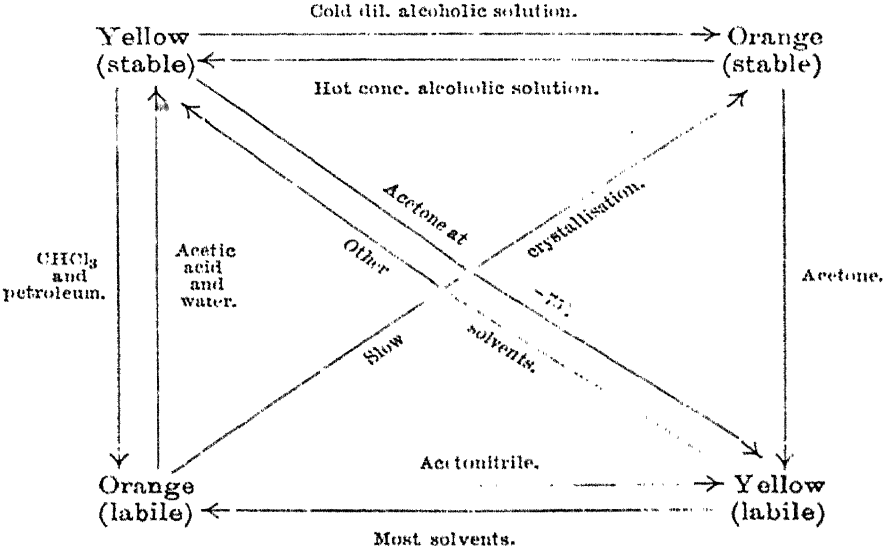
A further complication is introduced by the existence of different modifications having the same colour, and yielding optically identical solutions. To such a condition, which includes such familiar instances as the *syn-* and *anti*-oximes and other stereoisomerides,

54 A. Hantzsch and J. Heilbron, *Ber.*, 1910, **43**, 68 ; *A.*, i, 198.
55 A. Hantzsch and R. Robison, *ibid.*, 45, 92 ; *A.*, i, 196, 200.
56 A. Hantzsch and P. W. Robertson, *ibid.*, 106 ; *A.*, i, 203.

the name of "homochromoisomerism" is given. Both chromoisomerism and homochromoisomerism are observed in the nitroanilines, a good example being given by 2 : 4-dinitrophenyltolylamine,



the relations between the isomerides being shown in the following scheme [57]:



The two kinds of yellow solutions, although optically identical, deposit different yellow salts on crystallisation. The whole of the salts are unimolecular in solution.

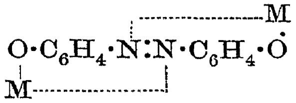
Azophenol is known to exist in two modifications, one of which, α-azophenol, obtained from *p*-nitrophenol, being green, and the β-modification, obtained from quinoneazine, being dark red. The colours become more nearly alike in their hydrates. It is now found [58] that distinct α- and β-salts exist, regenerating their parent substances. These salts are pantochromic, crystallising in yellow, red, and green modifications, so that a maximum number of six salts may be obtained from each metal. The α- and β-compounds are regarded as stereoisomerides:

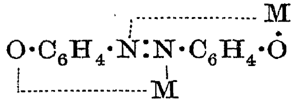
$$\begin{array}{r} OH\cdot C_6H_4\cdot N \\ \| \\ OH\cdot C_6H_4\cdot N \end{array} \qquad \begin{array}{l} OH\cdot C_6H_4\cdot N \\ \quad\quad\quad\quad\;\; \| \\ \quad\quad\quad\quad\;\; N\cdot C_6H_4\cdot OH \end{array},$$

and in accordance with this assumption both modifications yield

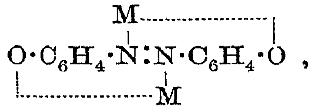
[57] A. Hantzsch, *Ber.*, 1910, **43**, 1651, 1662; *A.*, i, 474, 475.
[58] A. Hantzsch, *ibid.*, 2512; *A.*, i, 790.

optically identical solutions, whilst the respective salts also have identical absorption spectra. The difference in colour of the solid azophenols and their salts is attributed to valency-isomerism, the labile form passing into the more stable on dissolution. Formulæ for these isomerides are proposed, namely:



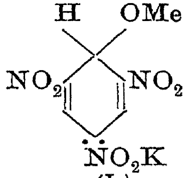


and

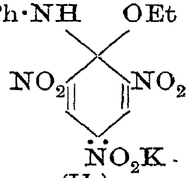


but, as in most similar instances, it is difficult to form a clear physical image of the conditions intended to be represented by such arrangements of subsidiary valencies.

It is known that the coloured salts of the colourless *s*-trinitrobenzene are not simple salts, but alcoholates, such as (I). The salts



(I.)



(II.)

of picrylaniline are found [59] to have a similar composition, the potassium salt in alcoholic solution, for example, having the formula (II). Some compounds of this class are capable of combining with two or three molecules of alkoxide, and as the resulting compound approaches more nearly to the saturated condition, the trialcoholate being a derivative of *cyclo*hexane, the colour becomes correspondingly lighter. Dinitro-compounds can form mono- and di-alcoholates.

Absorption Spectroscopy.—Attention has been once more directed to the spectroscopic method of investigating equilibria in substances exhibiting keto-enolic tautomerism. A very thorough study of ethyl acetoacetate and its derivatives and salts in a number of different solvents [60] leads to the conclusion that the selective absorption observed in solutions of the salts is not due to the enolic modification or to an oscillation between the ketonic and enolic conditions, but to an isomeric *aci*-form. Enolisation of the parent substance takes place to a varying extent in different solvents, in such a way that the proportion of ketone increases with the dielectric constant of the

[59] M. Busch and W. Kögel, *Ber.*, 1910, **43**, 1549; *A.*, i, 472.
[60] A. Hantzsch, *ibid.*, 3049; *A.*, i, 811.

solvent, but the absorption thereby produced is never selective. On the other hand, the solutions containing alkali always absorb selectively. The *aci*-modification must be derived from the enol, and the great difference in absorptive power excludes mere stereochemical *cis-trans*-isomerism. It thus becomes necessary to invoke the aid of the subsidiary valencies, and the following formulation is proposed:

$$\begin{array}{ccccc} \begin{array}{c} CH_3\cdot CO \\ CO_2Et\cdot CH_2 \end{array} & \rightleftarrows & \begin{array}{c} CH_3\cdot C\cdot OH \\ \| \\ CO_2Et\cdot CH \end{array} & \rightleftarrows & \begin{array}{c} CH_3\cdot C—OH \\ \| \quad \vdots \\ H\cdot C\cdot CO\cdot OEt \end{array} \\ \text{Keto.} & & \text{Enol.} & & \text{Aci.} \end{array}$$

the suggestion being made that the enol is only stable in the *trans*-configuration, whilst the *cis*-configuration at once passes into the *aci*-form. This stereochemical hypothesis is, of course, not an essential part of the explanation. The fact that the addition of successive quantities of alkali increases the absorption until a maximum is reached is explained as being due to the hydrolysis of the salts, which are only stable in the presence of a large excess of alkali, so that solutions which do not contain such an excess are composed to a large extent of the enol, which does not give rise to selective absorption.

The conclusions derived from the spectroscopic evidence as to the equilibrium between the ketonic and enolic modifications in different solvents are in general confirmed by determinations of the refractivity, and are also in accordance with the observed time-effects in the ferric chloride reaction, although the latter is not suitable for the quantitative study of the equilibrium.

Another long series of spectroscopic observations of compounds, many of which exhibit keto-enolic tautomerism, relates to camphor and its derivatives.[61] It is found that the simple ketones, such as camphor and its α-derivatives, absorb selectively to an extent which varies with the solvent and with the concentration. The form and position of the absorption band is quite independent of the tendency to undergo isomeric change, as shown by the mutarotation, and depends rather, as in other cases, on a particular distribution of residual affinity throughout the molecule. The application of considerations similar to those employed by Flürscheim[62] in the discussion of reactivity accounts satisfactorily for the position of the bands in many of the derivatives of camphor, the absorbing group being $>O{=}\underset{|}{C}{-}\underset{|}{C}{=}\underset{|}{C}{-}\underset{|}{O}<$. The case of nitrocamphor and its derivatives stands somewhat apart, and falls into relation with that of the aliphatic nitro-compounds, the great

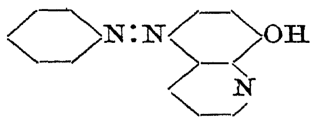
[61] T. M. Lowry and C. H. Desch, *Trans.*, 1909, **95**, 807, 1340; T. M. Lowry, C. H. Desch, and H. W. Southgate, *ibid.*, 1910, **97**, 899; T. M. Lowry and H. W. Southgate, *ibid.*, 905.

[62] *Ann. Report*, 1909, 60.

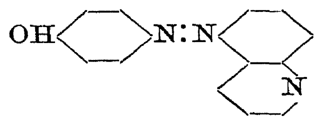
selective absorption observed in alkaline solutions being directly connected with the formation of a distinct *aci*-modification. An extensive series of aromatic nitro-compounds has also been examined spectroscopically,[63] with rather different results, the absorption being attributed to the influence of the unsaturated nitro-group on the pulsations of the ring, as modified by other substituents, and the quinonoid structure being rejected for the salts and *aci*-modifications. The principal argument in favour of this view is the appearance of the characteristic band at about the same concentration throughout a long series of compounds, some of which are incapable of receiving a quinonoid formulation, such as the dialkylated monoamines. The groups ·ONa, $\cdot NH_2$, and $\cdot NMe_2$, when associated with one or more nitro-groups in an aromatic compound, produce practically identical effects on the absorption, and as dinitrodimethylaniline, for example, cannot possibly be quinonoid, it is considered unnecessary to assume such a structure for the nitroanilines or the nitrophenoxides. As in several other researches referred to above, the influence of the residual affinity of the solvent employed on the position of the absorption band is very conspicuous in the published curves.

An extension of this work to nitrated azo-compounds leads to the result that the nitrobenzeneazophenols and their salts have entirely similar spectra, the absorption of the latter being shifted towards the red. *m*- and *p*-Nitrobenzeneazodimethylaniline resemble the alkali salts, this being a further argument against a quinonoid structure for the salts of the nitro-compounds.[64]

Two series of *p*-hydroxyazo-derivatives of quinoline (I and II) give spectra indicating that they have the azo-constitution, and are not quinonoid:



(I.)



(II.)

The dihydrochlorides of (I) are very unstable in comparison with those of (II), which is taken to indicate that the second molecule of hydrogen chloride is attached to oxygen rather than to carbon.[65]

Only the merest reference can be made to other spectroscopic investigations. A number of bases have been examined, the absorption spectra of the pure liquid in thin films, of the vapour, and of solutions in various solvents being observed, but it will evidently be necessary to accumulate a large quantity of data before

[63] E. C. C. Baly, W. B. Tuck, and Miss E. G. Marsden, *Trans.*, 1910, **97**, 571.
[64] E. C. C. Baly, W. B. Tuck, and Miss E. G. Marsden, *ibid.*, 1494.
[65] J. J. Fox, *ibid.*, 1337.

any general conclusion can be drawn, owing to the great differences exhibited by these spectra. The absorption spectrum of the vapour is often remarkably complex.[66] Other investigations relate to iodo-derivatives, and to a comparison of the groups ·N:N· and ·CH:CH·.[67]

Stereochemistry.

Recent work in stereochemistry has been confined, for the most part, to matters of detail, and no great advance in principle has to be recorded. Attempts to find a quantitative relationship between the degree of asymmetry of a molecule and its optical activity have met with little success, and the problem of the "asymmetry product" therefore receives less attention now than was the case a few years ago. A branch of study which properly falls under the head of stereochemistry, although unconnected with optical activity, is the establishment of relations between constitution and crystalline form, especially by means of Pope and Barlow's conception of valency volumes. The most important application of this doctrine to organic chemistry during the past year has been the examination of the sulphonyl chlorides and bromides of the 1 : 4-dihalogen derivatives of benzene,[68] an extensive series of measurements leading to results according very satisfactorily with the requirements of the hypothesis, but the details fall outside the scope of this report.

A great number of practical points in the study of optical activity have received attention. The observation that the activity of certain alkaloids does not correspond with that of their salts[69] indicates a possible source of error in working with optically active tertiary bases, against which it is necessary to take precautions.

Resolution.—It is well known that the process of resolution of externally incompensated acids or bases by crystallisation of their salts with an optically active base (or acid) is often, if not usually, complicated by the tendency of the salts *d*-acid + *d*-base and *d*-acid + *l*-base, to form crystals containing both individuals. Such mixtures may behave in one or more of three well-defined ways:

(1) Each crystal which separates may contain only one salt, in which case an easy separation may be effected by the method of Pope and Peachey. (2) The crystals may consist of a partly racemic

[66] J. E. Purvis, *Trans.*, 1910, **97**, 692, 1035, 1546, 1648; Miss A. Homer and J. E. Purvis, *ibid.*, 280; K. Schaefer, *Zeitsch. wiss. Photochem.*, 1910, **8**, 212, 257; *A.*, ii, 562.

[67] C. R. Crymble, A. W. Stewart, and R. Wright, *Ber.*, 1910, **43**, 1183, 1188, 1191; *A.*, ii, 470.

[68] H. E. Armstrong, *Trans.*, 1910, **97**, 1578; R. T. Colgate and E. H. Rodd, *ibid.*, 1585.

[69] F. H. Carr and W. C. Reynolds, *ibid.*, 1328.

"compound" of the two salts, and here no resolution by the foregoing method can be effected. (3) Each crystal may contain both salts, but in varying proportions; in other words, the salts form solid solutions in one another, and in this instance resolution is very slow and incomplete.

The resolution of externally compensated camphor-π-sulphonic acid with one-half an equivalent of strychnine forms an excellent example of the first type. An instance of type 3 has been observed, namely, that of the resolution of 1-methyl*cyclo*hexylidene-4-acetic acid by brucine; the separation of *d*-bornylamine from *d*-*neo*bornylamine by means of *d*-α-bromocamphor-π-sulphonic acid, and also of that of *d*-menthylamine from *d*-*iso*menthylamine by crystallisation of their mixed hydrochlorides are also complicated by the formation of solid solutions of the two component salts.[70]

Racemic Compounds.—An observation of recent date appears to offer unequivocal evidence in favour of the view that racemic compounds may exist in the liquid state or in solution, the rate of decomposition of camphorcarboxylic acid in acetophenone solution being 3 per cent. less when a mixture of the *d*- and *l*-acids is used than when either is present alone.[71]

The appearance of a maximum on the freezing-point concentration curve of mixtures of two optical isomerides is evidence of the formation of a stable racemic compound on solidification, and has been considered to afford a presumption that such a compound exists in the liquid mixtures. Such a maximum is strongly marked in the freezing-point curve of mixtures of *d*-, *l*-, and inactive α-pipecoline.[72] The solubility of dipentene is unaffected by the addition of one of its active components, and the same is true of *dl*-2-ethylpiperidine, from which the authors conclude that a racemic compound is not formed in these cases.

Asymmetry.—The case of methyl*cyclo*hexylideneacetic acid, synthesised and resolved into its enantiomorphous constituents, remains the only known case of a substance which owes its optical activity to molecular asymmetry and not to the presence of asymmetric atoms in the sense commonly understood. A substance which appears to be diphenylnaphthylallenecarboxylic acid,

$$\begin{matrix} C_6H_5 \\ C_{10}H_7 \end{matrix}\!\!>C{:}C{:}C<\!\!\begin{matrix} C_6H_5 \\ CO_2H \end{matrix},$$

has recently been synthesised[73]; this structure represents one of the simplest types of asymmetric molecules, but attempts to resolve the compound into its active constituents have not been successful.

[70] W. J. Pope and J. Read, *Trans.*, 1910, **97**, 987.
[71] K. Fajans, *Zeitsch. physikal. Chem.*, 1910, **73**, 25; *A.*, ii, 599.
[72] A. Ladenburg and Sobecki, *Ber.*, 1910, **43**, 2374; *A.*, i, 769.
[73] A. Lapworth and E. Wechsler, *Trans.*, 1910, **97**, 38.

A novel method of obtaining a substance having a molecule with an enantiomorphous constitution in virtue of the arrangement of groups attached to a silicon atom has proved successful. The starting point was dibenzylethylpropylsilicane, $SiEtPr(CH_2Ph)_2$; on sulphonation this yielded a mono- and a di-sulphonic acid, the former of which contained an asymmetrical silicon atom, and was finally resolved into its enantiomorphous components by means of brucine; the rotatory powers of the active forms were small, $[\alpha]_D$ being about 1°, but satisfactory evidence was adduced that a real resolution had been effected. Although but few cases of optically active silicon compounds have been obtained, it is certainly remarkable that all of them exhibit the true physical characteristics of enantiomorphous substances, but display only very feeble optical activity.[74]

Applications of Stereochemical Properties.—The synthesis of amidines, containing two different basic radicles, may result in the formation of one or other of the two possible isodynamic forms, $NR^1{:}CR{\cdot}NHR^2$ and $NR{\cdot}CR{:}NR^2$, or a mixture of both may be obtained. The former appears to be the case when the radicles R^1 and R^2 are dissimilar in character, and the latter when these radicles are closely related. This subject has recently been studied with the aid of optically active radicles, and it is found that the following formulæ represent stable compounds, $C_{10}H_{19}$ being the menthyl radicle:

$$C_6H_5{\cdot}NH{\cdot}CPh{:}N{\cdot}C_{10}H_{19} \text{ and } C_2H_5{\cdot}NH{\cdot}CPh{:}N{\cdot}C_{10}H_{19}.$$

When the radicle R and R_2 are identical in *chemical* character, it was to be expected that the two isomerides would be equally stable, and that each would constitute one-half of the product. This was confirmed by preparing an amidine, in which R and R_2 were *d*-bornyl and *l*-bornyl respectively when the product was found to be optically inactive, and therefore consisted of equal quantities of the two isomerides:

$$(l)C_{10}H_{17}{\cdot}NH{\cdot}CPh{:}N{\cdot}C_{10}H_{17}(d) \text{ and } (l)C_{10}H_{17}{\cdot}N{:}CPh{\cdot}NH{\cdot}C_{10}H_{17}(d).$$[75]

The ethylated compound was also inactive, and could not be resolved by crystallisation of its *d*-camphorsulphonate.

A further instance of the use of optically active compounds in the study of isodynamic isomerism is of interest, as bearing on the old controversy as to the constitution of the dichlorides of those dicarboxylic acids which readily yield internal anhydrides, such as those of the succinic and phthalic acid series. It was found that *l*-methoxysuccinyl dichloride, even when crystalline and

[74] F. Challenger and F. S. Kipping, *Trans.*, 1910, **97**, 149 755.

[75] J. B. Cohen and J. Marshall, *ibid.* 328

freshly prepared, did not exhibit mutarotation, even in presence of such a powerful agent as aluminium chloride or in closed tubes at 100°; it is therefore highly improbable that the compound exists in two isodynamic forms.[76]

The Walden Inversion.—The report on Stereochemistry for last year indicated in a concise manner the stage then reached by investigation in this subject. Comparatively few additional communications have appeared during 1910, but some of these represent most important advances.

It has previously been held that phosphorus pentachloride reacts normally with α-hydroxy-acids, or, in other words, causes no inversion of the special distribution of the groups around the α-carbon atom; the first exception to this rule has been observed in the case of α-hydroxy-β-phenylpropionic acid,

$$CH_2Ph\cdot CH(OH)\cdot CO_2H.$$

The *d*-acid is converted into a chloro-acid chloride, from which, by the action of moist calcium carbonate, impure *l*-hydroxyphenylpropionic acid is obtained. This appears to be the first instance in which phosphorus pentachloride behaves in an abnormal manner.[77] Thionyl chloride, on the other hand, behaves normally, and the *l*-hydroxy-acid is converted by this agent into the corresponding *l*-chloro-acid.[78]

The majority of acids which have been closely investigated in connexion with the Walden inversion have contained amidogen, hydroxyl, or halogen attached to an asymmetric carbon atom simultaneously with a hydrogen atom and a carbonyl group, thus:

$$\cdot C\begin{cases} OH \\ CO_2H. \\ H \end{cases}$$

Fischer and Scheibler, who studied the reactions of *l*-β-hydroxybutyric acid, $CH_3\cdot CH(OH)\cdot CH_2\cdot CO_2H$, found no evidence of the occurrence of any inversion in this case. More recently, active β-hydroxy-β-phenylpropionic acid, $OH\cdot CHPh\cdot CH_2\cdot CO_2H$, has been investigated with similar results, although slight racemisation was detected.[79] Acids with this type of grouping do not therefore appear to undergo inversion.

The corresponding β-amino-β-phenylpropionic acid and its esters, when treated with nitrous acid, are converted into the hydroxy-acids with some racemisation, but in this case, too, no Walden change occurs.[80] On the other hand, the derivatives of active α-hydroxy-

[76] T. Purdie and C. R. Young, *Trans.*, 1910, **97**, 1524.
[77] A. McKenzie and H. Wren, *ibid.*, 1355.
[78] A. McKenzie and G. W. Clough, *ibid.*, 2564.
[79] A. McKenzie and H. B. Humphries, *ibid.*, 121.
[80] E. Fischer, H. Scheibler, and R. Groh, *Ber.*, 1910, **43**, 2020; *A.*, i, 622.

substituent has the greatest influence, and the meta- and para-substituents a much less effect.

Solvent Influence.—Further work has appeared on the influence of solvents on the rotation of a dissolved substance. In a series of experiments, in which ethyl tartrate was used as the active substance,[88] phenol and *p*-nitrophenol are shown to exert a great solvent influence, which largely disappears in the corresponding ethers. On the other hand, *o*-nitrophenol has a small influence, which is increased when the phenolic group is alkylated. Two hydroxyl groups also have the greatest effect when in the *p*-position, and least in the *o*-position. *p*-Benzoquinone has less effect than a phenol, so that the evidence, so far as it goes, points to a quinonoid structure for *o*-nitrophenol in mixtures with ethyl tartrate.

An application of the fact of solvent influence to the analysis of mixtures has been made, and presents distinct advantages in certain cases in which chemical analysis is difficult to perform. Thus the quantitative estimation of benzene in *cyclo*hexane is difficult and troublesome, but by taking advantage of the fact that benzene is almost without influence on the rotation of ethyl tartrate, whilst *cyclo*hexane exerts a considerable depressing influence, the proportions of the two substances present in a mixture may be estimated within about 3 per cent. by the simple determination of the rotatory power of a mixture with a fixed proportion of the ester.[89]

In previous papers by Patterson and others, the possibility that solvent influence in certain cases is due to combination of the solvent with the solute has frequently been discussed, but direct evidence of the existence of such compounds in solution is, from the nature of the case, very difficult to obtain. By using diethyl diacetyltartrate as the active substance, it has been found possible[90] to determine the freezing-point curves of a number of binary systems, the second component of which is inactive. All these systems are proved to form simple eutectiferous series, whilst with mixtures of *l*-menthol with nitrobenzene, naphthalene, and anethole, indications are obtained of the possible existence of highly dissociated compounds. The absence of a maximum or of a distinct break in the freezing-point curve is, of course, not conclusive against the existence of compounds in the liquid at higher temperatures, but it affords a certain amount of evidence against their existence. Measurements of the viscosity and dilatation fail to give any evidence of combination, and it is evident that the materials for

[88] T. S. Patterson and Miss E. F. Stevenson, *Trans.*, 1910, **97**, 2110.
[89] T. S. Patterson and A. Fleck, *ibid.*, 1772.
[90] O. Scheuer, *Zeitsch. physikal. Chem.*, 1910, **72**, 513; *A.*, ii, 470.

a satisfactory theoretical discussion of the conditions in such solutions do not yet exist.

The measurement of the rotatory dispersion does not, as a rule, afford much information beyond that given by the simple rotation. Determinations of the dispersion of ethyl tartrate and of ethyl malate in a large number of solvents[91] show that, if the specific rotation in red light is higher than that of the pure ester, the rotation rises from red to blue, whilst it falls if the rotation was originally lower than that of the ester. Some of the solvents used were such as would react chemically with the esters used, and the results in such cases are obviously not comparable with the others.

Stereoisomeric Substituted Glutaconic Acids.—Glutaconic acid and many of its alkyl derivatives have been obtained in one form only, and this circumstance was adduced in favour of a dynamic formula for these substances, in which one of the α-hydrogen atoms, in the α-position, is imagined to be held in a state of suspense or vibratile motion between the two α-carbon atoms.[92] The existence of stereoisomerism among some of these compounds was afterwards demonstrated for the β-methyl derivative,[93] and more recently for a variety of other substituted glutaconic acids.[94]

The previously known forms are readily converted into anhydrides, which, on hydrolysis by the usual processes, at once give rise to the original acids; for this reason they have hitherto been mistaken for the *cis*-representatives. In reality the true *cis*-forms, corresponding with the anhydrides, are unstable towards the agents generally used for hydrolysis, and as soon as produced undergo a transformation into the original *trans*-acids, from which the anhydrides are prepared. The stability of the different forms of these acids is, however, greatly affected by the number and positions of the substituent groups in the molecule.

The isolation of the *cis*-forms can only be accomplished by carrying out the hydrolysis extremely carefully in presence of colloids (preferably casein), which appear to retard the stereoisomeric change.

Thus the two isomeric α-methylglutaconic acids are prepared from ethyl dicarboxymethylglutaconate by the action of aqueous alkali. The *cis*-form may also be obtained from the well-known *trans*-acid by converting the latter into its anhydride, and allowing it to absorb moisture from the air or by hydrolysing it with acids

[91] H. Grossmann, *Zeitsch. physikal. Chem.*, 1910, **73**, 148; H. Grossmann and B. Landau, *ibid.*, **75**, 129; *A.*, ii, 563, 1017.

[92] J. F. Thorpe, *Trans.*, 1905, **87**, 1669.

[93] F. Feist, *Annalen*, 1906, **345**. 60; *A.*, 1906, i, 334.

[94] F. Feist, *ibid.*, 1909, **370**, 41; F. Feist and G. Pomme, *ibid.*, 61, 72; F. Feist and R. Reuter, *ibid.*, 82; *A.*, i, 7, 9, 39.

or alkalis in presence of casein; it retains its configuration when fused, but it inverted by aqueous sodium hydroxide or hydrochloric acid.

Glutaconic acid itself has been obtained in only one form, and until its *cis*- and *trans*-forms have been isolated, the dynamic explanation of the behaviour of this and similar compounds is not likely to be discarded by those chemists to whom it appears to offer any theoretical advantages.[95]

The Cinnamic Acids.—The supposed existence of a number of isomeric cinnamic acids[96] is now only maintained by Erlenmeyer, and a quantity of evidence is being accumulated in support of the view that the *allo*- and *iso*-acids are dimorphic modifications. It is found[97] that most elaborate precautions are necessary to prevent accidental inoculation with crystals of one or other of the labile modifications during recrystallisation experiments, and that when such inoculation is most completely excluded, the product is almost always the stable *iso*-acid, melting at 42°. Solutions of these three acids are completely identical in electrical conductivity[98] and in their absorption spectra,[99] whether water or alcohol is used as the solvent, whilst a solution of the ordinary acid shows a small but distinct difference in the form of the absorption band.

The statement that ordinary synthetic cinnamic acid contains two isomerides, α- and β-heterocinnamic acid, which are not present in the acid from storax, has not been allowed to pass unchallenged, and a careful crystallographic study shows[1] that the marked differences of crystalline habit between the natural and the synthetic acids may be produced by the presence of a small quantity of the *o*-chloro-acid in the latter. Other impurities, such as *o*-nitrocinnamic acid, have a precisely similar effect. The α- and β-heterocinnamic acids are thus probably fractions in which the impurity has been concentrated. This explanation accords with the fact that the two supposed new acids melt at 128°, a few degrees lower than the pure acid, and although experiments are described[2] to prove that the differences persist in the absence of all such impurities, they are hardly conclusive, and it appears almost certain that the number of stereoisomeric cinnamic acids does not exceed the two required by theory.

[95] Compare A. F. Campbell and J. F. Thorpe, *Trans.*, 1910, **97**, 1299.

[96] *Ann. Report*, 1909, 133.

[97] C. Liebermann and H. Trucksäss, *Ber.*, 1909, **42**, 4659; 1910, **43**, 411; *A.* i, 36, 175.

[98] E. Biilmann and N. Bjerrum, *ibid.*, 1910, **43**, 568; *A.*, i, 346.

[99] H. Stobbe, *ibid.*, 504; *A.*, ii, 247.

[1] C. N. Riiber and V. M. Goldschmidt, *ibid.*, 453; *A.*, i. 174.

[2] E. Erlenmeyer and G. Hilgendorff, *ibid.*, 955, 1076; *A.*, i, 320, 383.

In order to confirm the generally accepted configurations of the ordinary and *allo*-acids by an entirely independent method, a reaction has been employed which is generally applicable to olefine acids.[3] Mercuric acetate yields complex mercury salts with the malenoid forms of such acids, and in the case of *allo*cinnamic acid forms an inner salt of α-mercuri-β-hydroxy-β-phenylpropionic acid,

$$OH\cdot CHPh\cdot CH<\begin{matrix} CO_2 \\ | \\ Hg \end{matrix}.$$

This acid is therefore regarded as having the *cis*-configuration, leaving the *trans*-configuration for the ordinary acid, which does not react under similar conditions.

The Stereochemistry of Nitrogen.

Although it is generally considered that the existence of isomeric compounds of the formula N*abc* has been disproved, the question of the configuration of molecules containing tervalent nitrogen possesses sufficient interest to serve as the motive of further investigations from time to time. Thus two isomeric compounds were described in 1896[4] as being obtained by the interaction of *m*-4-xylidine and acetaldehyde in dilute hydrochloric acid, and the similarity of the chemical properties was such that the isomerism was then attributed to the arrangement of the three groups about the central nitrogen atom:

$$C_6H_3Me_2-\underset{\displaystyle H}{\overset{}{N}}-CHMe\cdot CH_2\cdot CHO.$$

A re-investigation of these compounds[5] proves that their differences are really due to structural isomerism, and their chemical behaviour is best explained by assigning to the α-isomeride the formula given above, and to the less fusible and soluble β-form a closed-ring formula:

$$C_6H_3Me_2\cdot N<\begin{matrix} -CHMe- \\ CH(OH) \end{matrix}>CH_2.$$

Neither compound is converted into the other by the action of solvents or of heat, but an equilibrium mixture is produced by the action of acids. Certain differences in the behaviour of the two isomerides towards nitrous acid remain unexplained, and the absorption spectra are inconclusive.

Like the above, most compounds of the formula N*abc* are basic in character. A compound having acid properties has also been examined, the attempt being made to bring about a separation of

[3] E. Biilmann, *Ber.*, 1910, **43**, 568 ; *A.*, i, 346.

[4] W. v. Miller and J. Plöchl, *ibid.*, 1896, **29**, 1462 ; *A.*, 1896, i, 534.

[5] H. O. Jones, *Trans.*, 1910, **97**, 632 ; J. E. Purvis, *ibid.*, 644.

isomerides, if present, by the crystallisation of salts with active alkaloids.[6] This compound is 2 : 3 : 5-trinitro-4-acetylaminophenol,

$$CH_3{\cdot}CO{-}\underset{\large H}{\underset{|}{N}}{-}C_6H(NO_2)_3{\cdot}OH,$$

which forms a stable salt with brucine, but the acid compound liberated by acids from the brucine salt is found to be devoid of optical activity.

Amongst compounds containing quinquevalent nitrogen, those in which the nitrogen occurs in a piperidine ring have proved interesting, from the considerable influence of the size of the groups attached to atoms directly linked to the nitrogen atom on the asymmetry of the molecule.[7] Thus *dl*-6-phenyl-2-methyl-1-ethylpiperidine combines with allyl iodide, yielding two stereoisomeric quaternary ammonium salts.[8] In the course of the same investigation, an example of stereoisomerism in compounds of the type NXa_2bc, the nitrogen atom being a member of two rings, was observed. *o*-Xylylene bromide combines with 2-phenyl-6-methylpiperidine, and the product may be separated into two isomerides, differing in melting point and solubility, and yielding isomeric salts. These compounds contain only a single nitrogen atom, and thus differ from those previously obtained in isomeric forms from trimethylene bromide and dipiperidylethane, which contain two similarly situated nitrogen atoms[9]:

$$CH_2{<}\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}{>}\underset{\large Br}{\underset{|}{N}}{<}\begin{matrix}CH_2{\cdot}CH_2{\cdot}CH_2\\CH_2{-\!-\!-\!-}CH_2\end{matrix}{>}\underset{\large Br}{\underset{|}{N}}{<}\begin{matrix}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{matrix}{>}CH_2,$$

the present compounds having the constitution:

$$C_6H_4{<}\begin{matrix}CH_2\\CH_2\end{matrix}{>}\underset{\large Br}{\underset{|}{N}}{<}\begin{matrix}CHMe{\cdot}CH_2\\CHPh{\cdot}CH_2\end{matrix}{>}CH_2.$$

The case of compounds containing two asymmetric nitrogen atoms has been examined, in order to determine whether the same relations hold as in compounds containing two asymmetric carbon atoms. Thus, the compound:

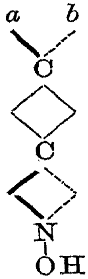
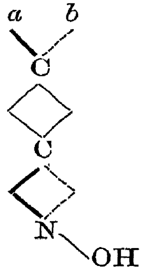
$$\begin{matrix}Ph\\Et\\Me\\I\end{matrix}{>}N{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}N{<}\begin{matrix}Ph\\Et\\Me\\I\end{matrix}$$

might be expected to exist in two inactive and two active modifications, the former being respectively the racemic and the internally compensated forms. The compound has, in fact, been synthesised in

[6] R. Meldola and H. Kuntzen, *Trans.*, 1910, **97**, 444.
[7] *Ann. Report*, 1909, 132. [8] M. Scholtz, *Ber.*, 1910, **43**, 2121 ; *A.*, i, 634.
[9] O. Aschan, *Zeitsch. physikal. Chem.*, 1903, **46**, 293 ; *A.*, 1904, i, 350.

two different ways, and in each case the product is a mixture of two inactive isomerides.[10] All attempts to resolve one of these isomerides into its active components by crystallising the camphorsulphonates or bromocamphorsulphonates, however, failed. The failure is of little weight as evidence against the racemic character of the compound, as the resolution of inactive dialkylsuccinic, dialkylglutaric, and dialkyladipic acids has also never been accomplished, and it is with these acids, rather than with the tartaric acids, that the nitrogen analogues are to be compared. Isomeric diquaternary ammonium salts of high molecular weight have not, so far, been isolated.

The Hantzsch-Werner Hypothesis.—The special form of stereoisomerism postulated by Hantzsch and Werner in order to account for the observed relations of the isomeric oximes, and rapidly extended to include the hydrazones and other compounds containing a :C:N· linking, has been accepted by many chemists with a certain reserve, arising from the difficulty of forming any clear mental picture of the forces constraining the molecule to assume the supposed configurations. The same, or even a greater, reluctance is felt to the extension of the hypothesis by Hantzsch to cover the diazotates and other compounds containing the ·N:N· linking. As regards the former class, however, no satisfactory alternative hypothesis has ever been proposed, the structural isomerism assumed in certain specific cases being clearly inapplicable in others. The Hantzsch-Werner hypothesis thus holds the field, but a special interest attaches to all cases of observed or predicted isomerism which serve to put its validity to the test. An instance of this kind is found in compounds of the type $\frac{a}{b}\!>\!C{:}C{:}N{\cdot}OH$, the molecule of which has a plane of symmetry or not according as the three valencies of the nitrogen atom lie in one plane or not.[11] Thus, whilst (I) is superposable on its mirror-image, (II) is not [12]:

I.  II. 

[10] E. Wedekind and O. Wedekind, *Ber.*, 1910, **43**, 2707; *A.*, i, 834.

[11] W. H. Mills and Miss A. M. Bain, *Trans.*, 1910, **97**, 1866.

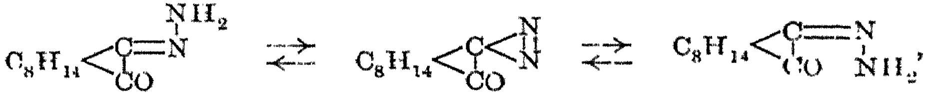
[12] The thick lines represent valencies lying in front of the plane of the paper, and the dotted lines valencies behind it.

As the practical difficulties of preparing such compounds would probably be very great, the device already employed by Perkin and others in the production of asymmetric molecules[13] has been adopted, namely, the substitution of the hexamethylene ring for the ethylene grouping $>C:C<$. The required conditions are fulfilled in the oxime of *cyclo*hexanone-4-carboxylic acid:

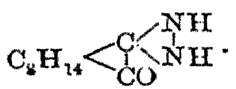
$$\begin{matrix} H \\ CO_2H \end{matrix}\!>C<\!\begin{matrix} CH_2\cdot CH_2 \\ CH_2\cdot CH_2 \end{matrix}\!>C:N\cdot OH:$$

and it is, in fact, found that this acid forms both dextro- and lævo-rotatory alkali salts, after resolution by means of morphine or quinine. The activity persists after conversion into the silver salts and decomposition with sodium chloride. The possibility that the active salts are really derived from a tautomeric form containing an asymmetric carbon atom is negatived by the chemical evidence, and the results lend considerable support to the view that the three valencies of the nitrogen atom are directed along the edges of a tetrahedron.

A further interesting instance is afforded by the semicarbazones, only very few of which have been definitely shown to exist in stereoisomeric modifications. A careful study of camphorquinonesemicarbazone[14] proves that two forms of this compound, mutually interconvertible by heating under suitable conditions, may be obtained. Dimorphism and polymerism are excluded, whilst a review of the types of structural isomerism which might conceivably be invoked to explain the differences shows that none of them are consistent with the chemical behaviour of the whole of the derivatives. The isomerism, in fact, extends to the semicarbazones, the simple hydrazones and their acyl derivatives, and the phenylcarbamylhydrazones, the relations between which are such as to admit of no doubt that the isomerism of each pair must be of the same kind. The fact that both hydrazones are obtainable from diazocamphor by reduction and are convertible into it by oxidation supports the hypothesis of stereoisomerism:



the chemical and optical properties of the hydrazones being inconsistent with the assumption that one of them has the constitution

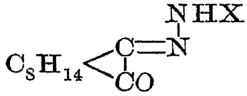


The β-modifications are slightly coloured, and as colour is

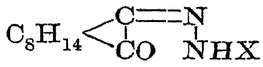
[13] *Ann. Report*, 1908, 106.

[14] M. O. Forster and A. Zimmerli, *Trans.*, 1910, **97**, 2156.

undoubtedly more likely to occur where there is a concentration of unsaturated atoms, the *syn*-configuration is assigned to the β-series and the *anti*-configuration to the α-series, thus:



α-Hydrazone, semicarbazone, and phenylcarbamylhydrazone.



β-Hydrazone, semicarbazone, and phenylcarbamylhydrazone.

A very simple example of stereoisomerism of this kind occurs in the chloroiminoketones. Whilst benzophenonechloroimide exists only in a single form, *p*-chlorobenzophenone forms two chloroimides:

$$\begin{matrix} C_6H_5\cdot C\cdot C_6H_4Cl \\ \| \\ N\cdot Cl \end{matrix} \quad \text{and} \quad \begin{matrix} C_6H_5\cdot C\cdot C_6H_4Cl \\ \| \\ Cl\cdot N \end{matrix}$$

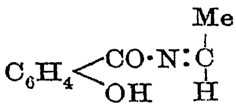
both of which react with hydrogen chloride to form *p*-chlorobenzophenonechloroimide, yielding *p*-chlorobenzophenone and ammonium chloride with water. Physical isomerism is excluded by the fact that each modification may be recovered unchanged after fusion or dissolution, whilst polymerism is excluded by the proof, in the case of the derivatives from *p*-methoxybenzophenone, that both forms have the simple molecular weight.[15]

Reference may also be made to two further instances that have been investigated recently. *p*-Toluidine reacts with the ketodichloride of *p*-chlorophenyl *p*-chlorostyryl ketone, yielding two isomeric arylimino-compounds[16]:

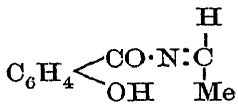
$$\begin{matrix} C_6H_4Cl\cdot C\cdot CH{:}CH\cdot C_6H_4Cl \\ \| \\ C_6H_4Me\cdot N \end{matrix} \quad \text{and} \quad \begin{matrix} C_6H_4Cl\cdot C\cdot CH{:}CH\cdot C_6H_4Cl \\ \| \\ N\cdot C_6H_4Me \end{matrix}$$

One of these is colourless, and the other yellow, and two corresponding series of isomeric salts are formed, but it is not possible at present to assign the respective configurations to the two isomerides. The matter is complicated by the fact that geometrical isomerism, due to the ethylene linking, although rejected by the authors, is possible, and also by the occurrence of a third labile modification under certain conditions.

The second instance is that of the ethylidenesalicylamides, in which a great difference of stability between the *syn*- and *anti*-modifications is observed[17]



syn.



anti.

[15] J. Stieglitz and P. P. Peterson, *Ber.*, 1910, **43**, 782 ; *A.*, i, 323.

[16] F. Straus and A. Ackermann, *ibid.*, 596 ; *A.*, i, 241.

[17] W. L. Hicks, *Trans.*, 1910, **97**, 1032.

On the other side must be set the negative result of attempts to obtain stereoisomeric keto-anils.[18] Deoxybenzoinanil, $\begin{matrix}Ph\cdot C\cdot CH_2Ph\\ \| \\ N\cdot Ph\end{matrix}$, was only obtained in a single form, whilst phenyl α-naphthyl ketoneanil, $\begin{matrix}Ph\cdot C\cdot C_{10}H_7\\ \| \\ N\cdot Ph\end{matrix}$, yielded two modifications, differing in melting point and crystalline form, but considered to be physical isomerides from their identity of colour, solubility, and chemical behaviour.

The stereoisomerism of simple azo-compounds has not hitherto been observed, but two modifications of azobenzene are stated [19] to have been obtained by distilling azoxybenzene with iron filings. Definite proof that the difference is one of stereoisomerism, and not of merely physical isomerism, is at present lacking.

Some Novel Practical Methods and General Reactions.

In addition to the matter dealt with elsewhere, the following unclassified observations should not be overlooked.

When saturated hydrocarbons are nitrated, a considerable amount of oxidation usually occurs, the proportion of nitro-compounds formed being greater the smaller the quantity or concentration of nitric acid. On this observation is based a method in which aluminium nitrate, $Al(NO_3)_3,9H_2O$, is used as nitrating agent; this salt melts at 73°, and is completely hydrolysed at 140°, so that between these two temperatures there should be a point at which the free nitric acid attains the strength most suitable for the nitration of a given hydrocarbon; *cyclo*hexane in closed tubes at 115—120° gives 56·7 per cent. of mononitro-compound, a yield exceeding the greatest obtained by using free nitric acid.[20]

Spongy copper, in presence of sodium hypophosphite, decomposes water, liberating hydrogen, or, in presence of nitro-compounds dissolved in alcohol, acts as a reducing agent, and in certain cases theoretical yields of amines are obtained.[21] This reagent is useful for the preparation of aminophenols.

Acid chlorides unite with many unsaturated open-chain and cyclic hydrocarbons in presence of aluminium chloride, the products being β-chloroketones:

$$R\cdot CO\cdot Cl + \dot{\underset{\cdot}{C}}:\dot{\underset{\cdot}{C}} = R\cdot CO\cdot\dot{\underset{\cdot}{C}}\cdot\dot{\underset{\cdot}{C}}\cdot Cl.$$

[18] M. Busch and F. Falco, *Ber.*, 1910, **43**, 2557; *A.*, i, 747.

[19] C. V. Gortner and R. A. Gortner, *J. Amer. Chem. Soc.*, 1910, **32**, 1294; *A.*, i, 790.

[20] S. S. Nametkin, *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 581; *A.*, i, 829.

[21] A. Mailhe and M. Murat, *Bull. Soc. chim.*, 1910, [iv], **7**, 952; *A.*, i, 830.

From these products, unsaturated ketones are obtained by the action of amines.[22]

Methyl and ethyl sulphates are now largely displacing the corresponding halogen compounds, being not only much cheaper, but also more reactive, compounds containing several amino- and hydroxy-groups often being completely alkylated by repeated treatment with these agents, either alone or in presence of alkali.[23] Even free acid amides and their thio-derivatives unite with methyl sulphate below 100°, yielding the methosulphates of the methylimino-ethers, from which sodium carbonate solution liberates the imino-ethers.[24]

The preparation of nitriles by Lett's method is improved by using a mixture of lead thiocyanate with the lead or zinc salt of the fatty acid; instead of lead thiocyanate, a mixture of lead ferrocyanide and sulphur may also be used, although in this case the yield is not quite so large.[25]

When ketones of the formula $O\colon CR_1R_2$ are allowed to remain in contact with ammonia in alcoholic solution, and the liquid then allowed to flow on to metallic sodium, primary and secondary amines, $NH_2\cdot CHR_1R_2$ and $NH(CHR_1R_2)_2$, are formed in considerable quantities. The imino-compounds, $NH\colon CR_1R_2$, are probably formed in the first instance, and subsequently reduced. Methylamine may be substituted for ammonia, and gives similar results.[26]

Aldehydes, when acted on by anhydrides of carboxylic acids in presence of sulphuric, hydrochloric, phosphoric, or oxalic acids at low temperatures, are not converted into Semmler's *enol*-acetates, but into the diacetates, $R\cdot CH(OAc)_2$.[27] The same appears to be true of aldehydes having the formula $CHR_1R_2\cdot CHO$, even in absence of mineral acids,[28] and the *enol*-acetates of these can only be prepared from the α-glycols, $OH\cdot CRR'\cdot CH_2\cdot OH$.

A method employed by O. Wallach[29] and his co-workers for the preparation of hydroxy-ketones and their derivatives from certain unsaturated hydrocarbons of the terpene series may suitably find a place here, as there seems reason to suppose that the method will be a somewhat general one. The hydrocarbon (I) is first converted into its nitrosochloride (II), which is then heated with sodium acetate dissolved in glacial acetic acid. In this way, an acetylated

22 G. Darzens, *Compt. rend.*, 1910, **150**, 707; S. Krapiwin, *Bull. Soc. Impér. Natur., Moscou*, 1908, 1; G. Darzens and H. Rost, *Compt. rend.*, 1910, **151**, 758; ., i, 322, 349, 856.

23 Compare R. Meldola, *Proc.*, 1910, **26**, 232.

24 M. Matsui, *Mem. Coll. Sci. Eng. Kyoto*, 1909-1910, **2**, 37; *A.*, i, 695.

25 E E. Reid, *Amer. Chem. J.*, 1910, **43**, 162; *A.*, i, 169.

26 K. Löffler, *Ber.*, 1910, **43**, 2031; *A.*, i, 611.

27 R. Wegscheider and E. Späth, *Monatsh.*, 1909, **30**, 825; *A.*, i, 825.

28 M. Tiffeneau, *Compt. rend.*, 1910, **150**, 1181; *A.*, i, 379.

29 *Annalen*, 1910, **374**, 217; *A.*, i, 569.

oxime (III), or unsaturated oxime, may be formed, from which hydrolysis generates the corresponding hydroxy-ketone (IV) or unsaturated ketone respectively:

$$\underset{\text{(I.)}}{>\mathrm{C{:}CH}-} \longrightarrow \underset{\text{(II.)}}{>\overset{\mathrm{Cl}}{\dot{\mathrm{C}}}\cdot\mathrm{C(:NOH)}-} \qquad \underset{\text{(III.)}}{>\overset{\mathrm{OAc}}{\dot{\mathrm{C}}}\cdot\mathrm{C(:NOH)}} \longrightarrow \underset{\text{(IV.)}}{>\overset{\mathrm{OH}}{\dot{\mathrm{C}}}\cdot\mathrm{CO}-}$$

A new brominating agent, which may sometimes prove convenient, is a solution of hypobromous acid, prepared by adding mercuric oxide and bromine alternately to cold water. Benzene and benzoic acid are readily brominated by this reagent. The observation was made in examining the action of bromine on keto-dimethylpyrimidine, the perbromide being converted into substitution derivatives by the action of water, an effect which was traced to the intermediate production of hypobromous acid.[30]

The generalisation, often quoted, that $\alpha\beta$-unsaturated acids do not yield lactones when heated with 62 per cent. sulphuric acid, is not without exceptions, as in certain instances they undergo isomeric change, and finally may be transformed quantitatively into lactones of the corresponding saturated γ-hydroxy-acids. This is the case, for example, with the β-methyl- and β-ethyl-pentenoic acids, which yield the corresponding β-alkylvalerolactones[31]:

$$\begin{array}{l}\mathrm{CH\cdot CO_2H}\\ \|\\ \mathrm{CMe\cdot CH_2Me}\end{array} \longrightarrow \left.\begin{array}{l}\mathrm{CH_2\cdot CO}\\ |\\ \mathrm{CHMe\cdot CHMe}\end{array}\right>\mathrm{O}.$$

Two new methods of preparing azoxy-compounds may be mentioned. Azobenzene may be oxidised directly to azoxybenzene by means of hydrogen peroxide,[32] and many amines may be oxidised to the corresponding azoxy-compounds by a warm alkaline solution of potassium ferricyanide.[33] Aniline-*p*-sulphonic acid may be oxidised in this manner, yielding the compound

$$\mathrm{SO_3Na\cdot C_7H_4\cdot N_2O\cdot C_6H_4\cdot SO_3Na}.$$

A further application of hydrogen peroxide is to the oxidation of monohydric phenols, the product being either a dihydric phenol or a quinone or a mixture of both compounds. The solution used must be a concentrated one, containing 30 per cent. of hydrogen peroxide.[34]

Grignard's Reaction.—The applications of Grignard's reagent are now so manifold that monographs devoted to the subject rapidly fall out of date. In addition to the case referred to under

[30] O. Stark, *Ber.*, 1910, **43**, 670; *A.*, i, 234.

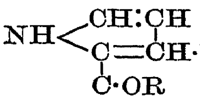
[31] F. Fichter and E. Gisiger, *ibid.*, 1909, **42**, 4707; F. Fichter, A. Kiefer, and W. Bernoulli, *ibid.*, 4710; *A.*, i, 88.

[32] A. Angeli, *Atti R. Accad. Lincei*, 1910, [v], **19**, i, 793; *A.*, i, 645.

[33] F. Reitzenstein, *J. pr. Chem.*, 1910, [ii], **82**, 252; *A.*, i, 702.

[34] G. G. Henderson and R. Boyd, *Trans.*, 1910, **97**, 1659.

unsaturated compounds (p. 71), mention may be made of the reaction between acyl chlorides and magnesium pyrryl iodide, resulting in the formation of ketones of the type:


[35]

Magnesium phenyl bromide reacts with substituted anilides in the following manner:

$$C_6H_5\cdot CO\cdot NEtPh + Ph\cdot Mg\cdot Br = \begin{array}{l} C\cdot Ph_2\cdot NEtPh \\ \dot{O}\cdot Mg\cdot Br \end{array},$$

this compound being decomposed by water into benzophenone and ethylaniline, but a second molecule of the reagent forms the stable compound $CPh_3\cdot NEtPh$.[36]

Remarkable differences are found in the triphenylmethyl series between the respective actions of magnesium phenyl chloride, bromide, and iodide.[37] Magnesium alkyl compounds do not in general react with phenyl ethers, but alkyl bromides, magnesium, and anisole or phenetole react together in benzene solution.[38]

The reactions occurring between magnesium organic compounds and various inorganic chlorides, etc., have also been studied. Only one atom in boron trichloride is replaced, and nitrogen chloride does not appear to react. Magnesium phenyl bromide and sulphur chloride yield phenyl disulphide, whilst thionyl chloride forms sulphoxides[39] and sulphides.[40]

Contact Actions of Metals and Inorganic Substances.

The employment of metallic oxides at high temperatures as contact materials for preparative purposes is still under investigation, and a résumé of the main results obtained with alcohols has now appeared.[41]

The method may be used for the preparation of mixed as well as simple ketones[42] and ethers,[43] both aliphatic and aromatic, and has

[35] B. Oddo, *Ber.*, 1910, **43**, 1012 ; *A.*, i, 426.
[36] M. Busch and M. Fleischmann, *ibid.*, 2553 ; *A.*, i, 728.
[37] J. Schmidlin, *ibid.*, 1137 ; J. Schmidlin and J. Wohl, *ibid.*, 1145 ; *A.*, i, 367, 368.
[38] V. Grignard, *Compt. rend.*, 1910, **151**, 323 ; *A.*, i, 669.
[39] W. Strecker, *Ber.*, 1910, **43**, 1131 ; *A.*, i, 532.
[40] V. Grignard and L. Zorn, *Compt. rend.*, 1910, **150**, 1177 ; *A.*, i, 532.
[41] P. Sabatier and A. Mailhe, *Ann. Chim. Phys.*, 1910, [viii], **20**, 289 ; *A.*, i, 606.
[42] J. B. Senderens, *Compt. rend.*, 1909, **149**, 995 ; 1910, **150**, 111, 702, 1336 ; *A.*, i, 11, 179, 318, 489.
[43] P. Sabatier and A. Mailhe, *ibid.*, 1910, **151**, 359, 492 ; *A.*, i, 668, 669.

various advantages as compared with the usual processes. Thiols are obtained when the vapour of the corresponding alcohol, mixed with hydrogen sulphide, is passed over heated metallic oxides,[44] especially good results being obtained with thorium oxide. The process is a continuous one, and the presence of hydrogen as an impurity in the hydrogen sulphide has not much effect on the yields obtained. Primary alcohols react at 300—360°, and are more satisfactory than the secondary; with phenols, a higher temperature (430—480°) must be used, and the yield of thiophenol never exceeds 17 per cent.

The use of aluminium sulphate as an aid in the dehydration of alcohols[45] possibly depends on a "contact action" of some kind. The preparation of unsaturated hydrocarbons and ethers from alcohols is greatly facilitated if about 5 per cent. of aluminium sulphate is present in the sulphuric acid used as dehydrating agent; ethylene may be prepared from ethyl alcohol at 138°, whilst ether is formed rapidly at 130°. Glycerol yields acraldehyde at 105—110° in presence of anhydrous or hydrated aluminium sulphate.[46]

Metallic sulphides, and in particular cadmium sulphide, at 320—330° cause a decomposition of thiols which is similar to that produced by metallic oxides on alcohols, dialkyl sulphides being formed; at 380°, more profound decomposition occurs, so that hydrogen sulphide and alkylenes are obtained.

In order to explain the action of metallic oxides, such as that of thorium or alcohol, it is suggested that a metallic alkyloxide is formed at an intermediate stage and subsequently decomposes. The equations given are as follows[47]:

(1) $ThO_2 + 2C_nH_{2n+1}\cdot OH = ThO(OC_nH_{2n+1}) + H_2O$.
(2) $ThO(OC_nH_{2n+1})_2 = ThO_2 + (C_nH_{2n+1})_2O$ (below 300°).
(3) $ThO(OC_nH_{2n+1})_2 = ThO_2 + 2C_nH_{2n} + H_2O$ (above 300°).

Numerous examples of the application of the reduction method of Sabatier and Senderens[48] are recorded, some of these being of considerable general interest; the temperature at which the nickel has been prepared appears to have considerable influence on its behaviour, and this is of special importance when the substances to be reduced are not easy to separate from the products.

Reference is made elsewhere in this report to experiments of

44 P. Sabatier and A. Mailhe, *Compt. rend.*, 1910, **150**, 1217, 1569; *A.*, i, 456, 536.
45 J. B. Senderens, *ibid.*, **151**, 392; *A.*, i, 649.
46 J. B. Senderens, *ibid.*, 530; *A.*, i, 651.
47 P. Sabatier and A. Mailhe, *ibid.*, **150**, 823; *A.*, i, 294.
48 G. Darzens, *ibid.*, 1909, **149**, 1001; *A.*, i, 63.

Henderson and others on the reduction of thymoquinol to menthanediol, leading to a simple synthesis of a terpene, and also on the reduction of camphene and bornylene; the temperature used is here, as in other cases, of considerable importance.

During reductions with hydrogen in presence of platinum-black at low temperatures, the activity of the platinum is often found to diminish after use; in this connexion, H. Fournier[49] finds that the activity of the metal may be restored by heating the latter for a few minutes at 100°. Working with ethereal solutions, this chemist has reduced crotonaldehyde to *n*-butyraldehyde and the corresponding alcohol, the two safroles to their dihydro-derivative, and the isomeric eugenols to dihydroeugenol.

Pinene is readily reduced by this method to a new hydrocarbon, $C_{10}H_{18}$; limonene yields an inactive hydrocarbon, $C_{10}H_{20}$. The product obtained from camphene is discussed in the section on the terpenes.

Willstätter's experiments on the application of this process to the preparation of saturated amino-compounds have been extended to the preparation of tropane from tropidine, and α-dimethylaminopentane from dimethylpiperidine. The undiluted base gives the best results in all cases.[50]

The use of colloidal palladium has been greatly simplified by modifying the method employed in its preparation. In place of protalbic acid or lysalbic acid, which were formerly used as the colloids needed to maintain the colloidal condition of the metal, gum arabic is used, and preliminary reduction of the palladium salt is not necessary. To the alcoholic solution of the substance which is to be reduced, aqueous solutions of palladium chloride and gum arabic are added, care being taken that the solution remains clear. Hydrogen is then forced into the solution under pressure, which may vary between $1\frac{1}{4}$ and 5 atmospheres. In this way, pulegone is readily reduced to menthone, with traces of menthol, mesityl oxide to methyl *iso*butyl ketone, and phorone to di*iso*butylcarbinol; oximes are reduced to amines, and aldehydes to alcohols.[51] The method promises to be among the most useful and selective reduction processes which the organic chemist has at his command.

Extended use is being made of small quantities of inorganic materials for the furtherance of certain reactions, which otherwise are very slow or require very high temperatures. It is already well known that the presence of small quantities of copper facilitates

49 *Bull. Soc. chim.*, 1910, [iv], **7**, 23; *A.*, i, 92.

50 R. Willstätter and E. Waser, *Ber.*, 1910, **43**, 1176; *A.*, i, 366.

51 A. Skita, *ibid.*, 1909, **42**, 1627; *A.*, 1909, i, 1627; A. Skita and H. Ritter, *ibid.*, 1910, **43**, 3393; *A.*, 1911, i, 71; compare also *Ann. Report*, 1909, 77.

the interaction of aromatic amines with aromatic halogen compounds, and it has recently been ascertained that the displacement of the hydrogen in aromatic amines by metallic sodium occurs more readily and at a comparatively low temperature if a heavy metal, such as copper, or a salt of a heavy metal, is present.

Synthesis of Hydrocarbons.—The subject of the direct union of carbon and hydrogen has received further attention. J. N. Pring[51a] now admits the direct union of these elements with the formation of methane at all temperatures above 1100°. The rate of union and, particularly, the rate of decomposition of methane are both too slow for equilibrium to be attained experimentally in the absence of a catalyst. With the addition of platinum to the carbon, the equilibrium is reached at 1200° and at 1500°. Above this temperature a rapid increase in the amount of methane occurs, owing to the decomposition of acetylene then formed in small amount. Bone and Coward[52] have given details of further experiments showing a 95 per cent. conversion of carbon into methane at 1150°. The carbon was mixed with 4 per cent. of its weight of platinum. Incidentally, they draw attention to the improbability of Ipatieff's statement[53] that ethylene is formed when a mixture of carbon monoxide and hydrogen is passed over coke mixed with reduced nickel, since 8 per cent. of ethylene in a gas mixture is stated not to be absorbed by either bromine or bromine water.

The Origin of Petroleum.

The mode in which paraffins and petroleum are produced in nature has long been a favourite subject of controversy, and is perhaps not yet satisfactorily explained. The naphthenes, which frequently occur with these, and contain ring structures with a smaller proportion of hydrogen atoms, have been considered by some to have their origin in the polymerisation of olefines, and Aschan actually observed the production of naphthenes together with "lubricating oil" when amylene is acted on by aluminium chloride. The question of the process by which naphthenes are formed has recently been the object of further investigation, and has been discussed at some length.[54] The conclusion is drawn that these compounds are not produced by any simple polymerisation alone; polyolefines are probably formed in the first instance, and these, owing to the presence of labile hydrogen, decompose into

[51a] *Trans.*, 1910, **97**, 498, compare Pring and Hutton; *ibid.*, 1906, **89**, 1591, and *Ann. Report*, 1906, 73.

[52] *Trans.*, 1910, **97**, 1219.

[53] *Ann. Report*, 1909, 77.

[54] C. Engler and O. Routala, *Ber.*, 1910, **43**, 388; C. Engler and B. Halmai, *ibid.*, 397; C. Engler, *ibid.*, 405; *A.*, i, 160.

paraffin, lubricating oils, and naphthenes. Amylene, with aluminium chloride at low temperatures, gives compounds of the first two types, but when these are more strongly heated, the lubricating oils partly decompose, giving naphthene. Amylene, heated under pressure, gives methane and hydrogen; when left with aluminium chloride in the cold, it is converted very largely into an oil which in composition and general character agrees closely with natural lubricating oil, C_nH_{2n-6}. Engler has also discussed the origin of the various hydrocarbons in nature, and suggests that the action of heat on partly fossilised plant and animal remains leads to the appearance of paraffins and olefines, which, under pressure, undergo more or less gradually the series of changes traced above. This accounts in a satisfactory way for the fact that natural oils, containing much lubricating oil, are usually rich in naphthenes.

A closely allied subject, namely, the pyrogenetic decomposition of naphtha, has also been investigated.[55] The formation of aromatic hydrocarbons is ascribed to the intermediate formation of acetylene and its polymerides, and in agreement with this view it is found that the proportion of benzene formed from naphtha at high temperatures is greatly augmented by the presence of those contact substances, such as iron gauze, which increase the speed of polymerisation of acetylene. With reduced nickel, iron, or ferric oxide, pumice, etc., at 600—700°, hydrocarbons, such as represent the main constituents of naphtha or coal gas, are said to be very largely decomposed into hydrogen and carbon.

A communication [56] on "The Volatile Constituents of Coal" will probably attract general notice. The results may be summarised as follows: (1) With all types of coal there is a well-defined point lying between 700° and 800°, which corresponds with a marked increase in the quantity of hydrogen evolved; this increase falls off in the case of bituminous coals above 900°, but it persists with anthracite coals up to 1100°. (2) Evolution of hydrocarbons of the paraffin series practically ceases at temperatures above 700°. (3) Ethane, propane, and butane, with, probably, higher members of the paraffin series, form a large percentage of the gas below 450°. Attention is drawn to certain technical developments which the results foreshadow, but these points lie without the scope of this report. The authors make a further suggestion which is of a more purely scientific kind, namely, that the temperature at which the hydrogen increases in amount corresponds with the decomposition point of a substance common to all coals.

[55] I. von Ostromisslensky and T. Burschanadze, *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 195; *A.*, i, 309.

[56] M. J. Burgess and R. V. Wheeler, *Trans.*, 1910, **97**, 1917.

New Binary Carbon Compounds.

When thiocarbonyl chloride, $CSCl_2$, is mixed with nickel carbonyl, a fall in temperature is observed, while carbon monoxide, nickel chloride, and a brown solid are formed. The latter appears to be a polymeric form of carbon monosulphide, CS, and in certain respects agrees in properties with the compound described by Sidot as a product of the decomposition of carbon disulphide by sunlight. A similar substance can be obtained by the action of ultra-violet light on carbon disulphide at -80°. At the temperature of liquid air, and at low pressures, carbon disulphide vapour, subjected to the silent electrical discharge, yields a small quantity of a gaseous product which detonates violently when the temperature rises, yielding a brown deposit; the gaseous product is comparatively stable at high temperatures in presence of excess of carbon disulphide vapour. It is inferred that the carbon disulphide is decomposed by the discharge into sulphur and a gaseous or very volatile endothermic carbon monosulphide, which polymerises with explosive violence at temperatures slightly above the boiling point of liquid air.[57]

Carbon disulphide and nickel carbonyl in the liquid state do not interact with appreciable speed, but when they are mixed in the state of vapour, a change occurs at the ordinary temperature, and even down to -80°. The interaction increases in speed as the pressure decreases, and thus resembles the oxidation of phosphorus and of aldehyde vapour in dry oxygen; moreover, the change appears to cease after a time. The latter effect is found to be due to carbon monoxide, which is one of the products; it is suggested that nickel carbonyl vapour is dissociated to some extent at ordinary and lower temperatures, the free nickel having a definite small concentration. As the equilibrium equation $Ni(CO)_4 \rightleftharpoons Ni + 4CO$ indicates that the concentration of the free nickel in vapour of the carbonyl should be inversely as the fourth power of the concentration of the carbon monoxide, it is evident that any time reaction in which the dissociated nickel takes part will be extremely sensitive to the presence of excess of carbon monoxide.[58]

Considerable general interest attaches to the discovery of a new carbon subnitride, C_4N_2,[59] which is prepared by removing the elements of water from the diamide of acetylenedicarboxylic acid, and therefore is probably the dinitrile of this acid (dicyano-

[57] Sir J. Dewar and H. O. Jones, *Proc. Roy. Soc.*, 1910, A, **83**, 408, 526; *A.*, ii, 408.

[58] Sir J. Dewar and H. O. Jones, *Trans.*, 1910, **97**, 1226.

[59] C. Moureu and J. C. Bongrand, *Compt. rend.*, 1910, **150**, 225; *A.*, i, 159.

acetylene), $CN \cdot C \vdots C \cdot CN$. It has an irritating odour, resembling that of cyanogen, and is spontaneously inflammable at 130°; its refractive and dispersive powers are considerably larger than those calculated by the usual rules for a substance having the foregoing constitution, and this is doubtless due to the conjugation of three triple linkings.

Nitroacetonitrile.

At one period, fulminic acid was represented by almost universal consent as nitroacetonitrile, $NO_2 \cdot CH_2 \cdot CN$, a view first suggested by Kekulé mainly in explanation of the ease with which mercury fulminate was converted by chlorine into trichloronitromethane, cyanogen chloride, and mercuric chloride. The synthesis of nitroacetonitrile, after innumerable unsuccessful attempts by various investigators, has recently been accomplished, and this result, were it for its historical associations alone, can hardly fail to awaken a very general interest.

The end was attained by removing the elements of water from methazonic acid, $C_2H_4O_2N_2$. The latter, which is a product of the interaction of hydroxylamine and sodionitromethane, yields potassium nitroacetate with aqueous alkalis, and is almost certainly *syn*-β-nitroacetaldoxime, $NO_2 \cdot CH_2 \cdot CH \colon NOH$; by the action of thionyl chloride in boiling ethereal solution, it is converted into nitroacetonitrile,

$$NO_2 \cdot CH_2 \cdot CH \colon NOH \longrightarrow NO_2 \cdot CH_2 \cdot CN + H_2O.$$

It is hardly necessary to say that the product has none of the most characteristic properties of fulminic acid, but exhibits the reactions of a primary nitro-compound when subjected to Konowaloff's test or when treated with nitrous acid, which converts it into cyanomethylnitrolic acid. The presence of the cyano-group is proved by the transformation of the substance into nitroethenylamido-oxime, $NO_2 \cdot CH_2 \cdot C(NH_2) \colon NOH$, with hydroxylamine, and into nitroacetamide by means of hydrogen chloride in methyl alcohol.

Carbohydrates and their Allies.

In extension of electrolytic investigations on the supposed reversibility of the sugar synthesis discussed in the report for last year (p. 81), the products obtained by the action of the hydroxides of lead and of sodium on aqueous sugar solutions have been examined; the substances isolated or identified include formaldehyde, pentoses, acetylcarbinol, acetylmethylcarbinol, and polyhydroxy-acids. This is held to confirm the view that the synthetic formation of sugar is of a reversible character; further, it is inferred that pentoses are intermediate phases in the synthetic process. Degradation of sugar to formaldehyde and pentose appears to occur

in solutions which have an alkalinity corresponding with that of the blood.[60]

It is interesting that lævulose, but not aldoses, undergoes profound change when their aqueous solutions are subjected to the influence of ultra-violet light, formaldehyde, methyl alcohol, and oxides of carbon being among the products obtained.[61]

An electrolytic method has been used for passing from one aldose having n carbon atoms to one having $n-1$ carbon atoms. The aldose is converted into the corresponding acid, which is then electrolysed:

$$OH\cdot CH_2\cdot[CH\cdot OH]_n\cdot CH(OH)\cdot CO_2H \rightarrow OH\cdot CH_2\cdot[CH\cdot OH]_n\cdot CHO,$$

and all the steps in the degradation of glucoheptose to formaldehyde may be traversed.

d-Galactonic acid, by this process, was converted into *d*-lyxose, *dl*-erythronic acid into *dl*-glyceraldehyde, glyceric acid into glycollaldehyde, and glycollic acid into formaldehyde. Aminohydroxy-acids, such as *iso*serine, appear to undergo a similar change.[62]

A lengthy treatise on the action of alkalis on sugars is hardly suitable for full discussion in the short space which can be devoted to it here, although, like all communications from the pen of its author, it bristles with interesting experimental and theoretical points. The suggestion is made that hexoses are never formed by a synthetic process from pentoses and formaldehyde, a view which is in striking contrast to that expressed by Löb and Pulvermacher, referred to above; the formation of these two substances from a hexose has never come under the author's observation, the normal products being either diose + tetrose, or two molecules of glyceraldehyde.

In certain cases, as, for example, with pentoses, it is suggested that an $\alpha\beta$-dienol is formed, $OH\cdot CH:C(OH)\cdot(CH\cdot OH)_2\cdot CH_2\cdot OH$; this is resolved into a tetrose and the hypothetical hydroxymethylene, $OH\cdot CH:$, which then condenses to the dienol, $OH\cdot CH:CH\cdot OH$, from which glycollaldehyde is formed. Tetroses yield only 2:3-dienols, and thus give rise to two molecules of diose and no triose; the same is supposed to hold with mannose, dextrose, and lævulose.

The author's theory of bivalent carbon is thus introduced in a most ingenious manner, but this application of it, in conjunction with the great disparity in properties assigned to pentoses on the

[60] W. Löb and G. Pulvermacher, *Biochem. Zeitsch.*, 1909, **23**, 10; 1910, **26**, 231; *A.*, i, 95, 609.

[61] H. Bierry, V. Henri, and A. Ranc, *Compt. rend.*, 1910, **151**, 316; *A.*, i, 652.

[62] C. Neuberg, L. Scott, and S. Lachmann, *Biochem. Zeitsch.*, 1910, **24**, 152; *A.*, i, 218.

one hand, and to hexoses and tetroses on the other, conveys the impression that an equally good explanation of the facts might be developed on more orthodox lines.[63]

The aldehexoses are oxidised by hydrogen peroxide in alkaline solution, the products being very different from those which are formed when air, Fehling's solution, or mercuric oxide is used as oxidising agent; in the latter instance, as was shown by Nef,[64] the substances obtained and their relative proportions are the same in each case. With hydrogen peroxide, dextrose and lævulose yield only formic acid, carbon dioxide, glycollic acid, and *α*-hydroxymethyl-*d*-arabonic acid (I); galactose yields the first three of these, with *α*-hydroxymethyl-*d*-lyxonic acid (II).

$$\begin{array}{rcccl} & CH_2\cdot OH & OH & OH & \\ CO_2H\cdot & C & —C & —C & \cdot CH_2\cdot OH \\ & OH & H & H & \end{array} \qquad \begin{array}{rcccl} & CH_2\cdot OH & H & OH & \\ CO_2H\cdot & C & —C & —C & \cdot CH_2\cdot OH \\ & H & OH & H & \end{array}$$

(I.) (II.)

These products are considered to be formed by the selective oxidation, in the alkaline sugar solution, of formaldehyde, glycollaldehyde, "*α*- and *β*-*d*-glutose" (from dextrose and lævulose) pro-

$$\begin{array}{rcccl} & OH & OH & OH & \\ OH\cdot CH_2\cdot & C & —CO\cdot C & —C & \cdot CH_2\cdot OH \\ & H & H & H & \end{array} \qquad \begin{array}{rcccl} & H & OH & OH & \\ OH\cdot CH_2\cdot & C & —CO\cdot C & —C & \cdot CH_2\cdot OH \\ & OH & H & H & \end{array}$$

(*α*-Glutose.) (*β*-Glutose.)

duced from the original sugars by the alkali. In the case of galactose, the isomerides oxidised must be *α*- and *β*-galtose.

The production of hydroxymethylarabonic acid from glutose is assumed to be due to an intramolecular change (analogous to the benzylic acid transformation) in the osone, which is the primary oxidation product:

$$OH\cdot CH_2\cdot CO\cdot CO\cdot CH(OH)\cdot \longrightarrow \begin{array}{l} CO_2H \\ OH\cdot CH_2 \end{array}\!\!>C(OH)\cdot CH(OH)\cdot$$

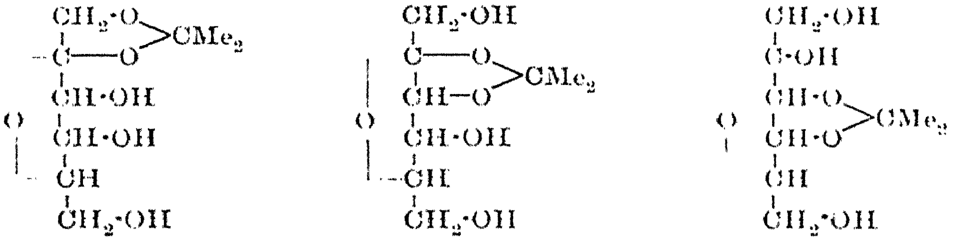
A re-examination of the acids obtained by oxidising dextrose and lævulose with hydrogen peroxide, in the presence of ferrous sulphate, makes it appear probable that previous observers were mistaken in supposing erythronic acid to be formed; formic, carbonic, and oxalic acids were isolated, and the remaining acids appeared to be ketonic in character. The large quantity of oxalic acid produced is attributed to hydrolysis of polyhexosones, such as

$CHO\cdot CO\cdot CO\cdot CO\cdot CH(OH)\cdot CH_2\cdot OH$.[65]

The Mode of Condensation of Acetone with Fructose.—It has

[63] J. U. Nef, *Annalen*, 1910, **376**, 1; *A.*, i, 711.
[64] *Annalen*, 1907, **357**, 214; *A.*, 1908, i, 5.
[65] H. A. Spoehr, *Amer. Chem. J.*, 1910, **43**, 227; *A.*, i, 221.

previously been shown that the aldol-like condensation products of acetone with lævulose consist mainly of α- and β-fructosediacetone, and that in the former of these at least the $CH_2\cdot OH$ group remote from the "ketonic" group of the lævulose molecule is intact.[66] The latter characteristic is shared by the fructosemonoacetones, which have now been isolated. Assuming that the rings present in all these compounds are of the five-membered type, $\mathrm{CMe_2}\!<\!\begin{matrix}\mathrm{O\cdot C:}\\ \mathrm{O\cdot C:}\end{matrix}$, the new compounds must have the constitutions (*A*) and (*B*); no substance of the third possible type (*C*) has been detected:



(*A.*) (*B.*) (*C.*)

It is concluded that the fructosediacetone is formed exclusively from *A*, for the acetone residues in fructosediacetone are found in the positions separately indicated in *A* and *C* respectively; the compound *B* is evidently not prone to further condensation, a conclusion consistent with the view that the acetone, $>CMe_2$, residue replaces the hydrogen atom of two adjacent hydroxyl groups.[67]

The mutarotation of the polyhydroxy-acids derived from the aldoses has recently been studied, and it is suggested that this may be utilised as a means of identifying the acids of the sugar group. A freshly prepared solution of arabonolactone has $[\alpha]_D$ about $-70°$; the rotatory power changes and becomes constant at $[\alpha]_D$ $-51{\cdot}5°$, a value identical with that which galactonic acid finally attains in aqueous solution, though originally it has $[\alpha]_D$ $-10°$. Gluconic, galactonic, saccharic, and rhomnonic acids and their lactones exhibit characteristic changes of the same type.[68]

Employing the synthetic method described in last year's report[69] for the preparation of disaccharides, a step towards the artificial production of a tetrasaccharide has been made. Bromoacetomaltose was shaken with dry silver carbonate in chloroform, when a substance, having the composition $C_{24}H_{28}O_7(OAc)_{14}$, of a tetradecaacetyldisaccharide was produced and isolated as an indistinctly

[66] Compare *Ann. Report*, 1909, 81.

[67] J. C. Irvine and C. S. Garrett, *Trans.*, 1910, **97**, 1277.

[68] K. H. Böddener and B. Tollens, *Ber.*, 1910, **43**, 1645; *Zeitsch. Ver. deut. Zuckerind*, 1910, 727; *A.*, i, 460.

[69] *Ann. Report*, 1909, 82.

crystalline powder; on hydrolysis, however, it was partly resolved, but there was present in the product a non-reducing carbohydrate of high molecular weight, probably the free tetrasaccharide. This paper also contains an interesting account of the preparation of menthylmaltoside and other synthetic "glucosides."[70]

The Constitution of the Benzenepolycarboxylic Acids.

Attention may here be directed to a communication of much importance[71] on this subject. The constitution assigned to numerous products obtained from terpenes and other ring compounds depends on the identification of their degradation products, among which are not infrequently found compounds such as the trimethylbenzenecarboxylic acids, and the structure of these, as well as that of the related benzenetetracarboxylic acid, is for the first time placed on a sound experimental basis. "Prehnitic acid" is shown to be 1 : 2 : 3 : 5-benzenetetracarboxylic acid, whilst "mellophanic acid" is the corresponding 1 : 2 : 3 : 4-compound. The interchange of the formulæ assigned to these two acids is justified, first, by the synthesis of the former from bromomesitylene, magnesium and carbon dioxide in ethereal solution, and the preparation of the latter by oxidation of 1 : 4-dimethylnaphthalene; moreover, the behaviour of the two acids, when subjected to dehydration or esterification, is not in harmony with the old view of their structures, but is in no way at variance with the formulæ now proposed.

Carbon Ring Formation.

It is well known that γ-ketonic carboxylic esters contain a $\cdot CH_2 \cdot$ group directly attached to the carbonyl group, and yield derivatives of 1 : 3-diketo*cyclo*pentane (3-hydroxy*cyclo*pentenone) on treatment with sodium or sodium alkyloxides; similarly constituted δ-ketocarboxylic esters yield derivatives of dihydroresorcinol. It has recently been found that ϵ-ketocarboxylic esters of the type (I) are converted into 2-acyl*cyclo*pentanones (II), and not into derivatives of diketo*cyclo*heptane (III):

$$\begin{array}{l} CH_2\cdot CH_2\cdot CO_2Et \\ | \\ CH_2\cdot CH_2\cdot CO\cdot CH_3 \end{array} \qquad \left.\begin{array}{l} CH_2 - CH_2 \\ | \\ CH_2\cdot CHAc \end{array}\right> CO \qquad \left.\begin{array}{l} CH_2\cdot CH_2\cdot CO \\ | \\ CH_2\cdot CH_2\cdot CO \end{array}\right> CH_2$$

(I.) (II.) (III.)

ζ-Ketonic esters may give *cyclo*hexanones, but never diketo*cyclo*octanes, whilst η-ketonic esters do not yield cyclic compounds at all.[72] Thus, the Dieckmann reaction is apparently not applicable

[70] E. Fischer and H. Fischer, *Ber.*, 1910, **43**, 2521 ; *A.*, i, 716 ; compare, also, E. Fischer and G. Zemplén, *ibid.*, 2536 ; *A.*, i, 718.

[71] Miss H. Bamford and J. L. Simonsen, *Trans.*, 1910, **97**, 1904.

[72] E. E. Blaise and A. Koehler, *Bull. Soc. chim.*, 1910, [iv], **7**, 710 ; *A.*, i, 626.

to the formation of rings other than those containing five or six carbon atoms.

A very remarkable compound, which from its mode of preparation would seem to be diethyl *cyclo*undecane-1 : 1-dicarboxylate:

$$\begin{matrix} CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2 \\ | \\ CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2 \end{matrix}\!\!>C(CO_2Et)_2,$$

has been obtained by the action of $\alpha\omega$-dibromodecane on ethyl sodiomalonate.[73] Whilst the existence of such an eleven-carbon ring is not at variance with Baeyer's strain theory as applied to van't Hoff's conception of the carbon atom and its complexes, yet no compound containing a ring of this magnitude and without a "bridge" has previously been obtained. Isomeric changes, leading to the formation of smaller rings in similar cases, are not quite unknown among nitrogenous compounds, and such a possibility in this case does not yet appear to have been entirely eliminated. Hardly less remarkable than the foregoing substance, if the constitution assigned to it be accepted, is another ester which has been described during the year.[74] It may be obtained from ethyl sodiocarboxyglutaconic ester by the action of iodine and in other ways; it is considered to possess the following structure, and in accordance with Baeyer's notation it is named, by its discoverers, ethyl 2 : 2 : 4 : 4-tetracarboxydi*cyclo* 011-butane-1 : 3-dimalonate:

$$CH(CO_2Et)_2\cdot C\!\!<\!\!\begin{matrix} C(CO_2Et)_2 \\ C(CO_2Et)_2 \end{matrix}\!\!>\!\!C\cdot CH(CO_2Et)_2.$$

A number of its derivatives have been prepared, all of which can be formulated on similar lines.

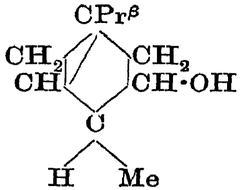
Carbon Ring Stability.

In the report of last year, reference was made to one or two instances in which apparently small alteration in the groups to a closed carbon chain had been found to alter profoundly the stability of the cyclic arrangement of atoms. O. Wallach had previously discussed certain changes of this kind,[75] in connexion with the behaviour of thujyl alcohol (I) and sabinene hydrate (II), the former of which is not affected when shaken with dilute sulphuric acid, whilst the latter is converted first into Δ^1-*p*-menthen-4-ol (III), and then into *p*-menthan-1 : 4-diol:

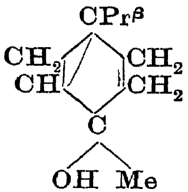
[73] A. Franke and O. Hankam, *Monatsh.*, 1910, **31**, 177; *A.*, i, 460.

[74] M. Guthzeit and E. Hartmann, *J. pr. Chem.*, 1910, [ii], **81**, 329; *A.*, i, 386.

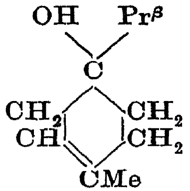
[75] *Annalen*, 1908, **360**, 83; *A.*, 1908, i, 429.



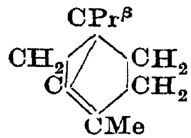
(I.)



(II.)



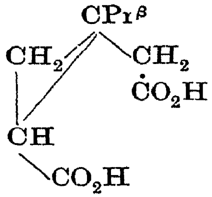
(III.)



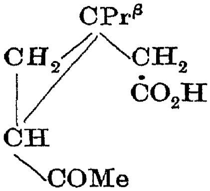
(IV.)

In explanation of such observations, it was suggested that the presence of a quaternary carbon in a ring leads to decreased stability, and in the foregoing instance dehydration of (II) would first yield a hydrocarbon having the constitution (IV), in which the quaternary carbon atom probably determines the instability of the *cyclo*propane ring. A similar explanation has been given[76] for the behaviour of α-thujadicarboxylic (V) and α-thujaketonic (VI) acids.

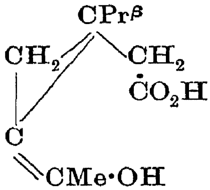
Ketones enolise far more readily than do carboxylic acids, so that (VI) may afford the isomeric enolic form (VII) under conditions where (V) would not be affected to any appreciable extent. The *cyclo*propane ring in the enolic form (VII) conforms to the above criterion of instability, and, in harmony with the theory, β-thujaketonic acid (VIII) is produced:



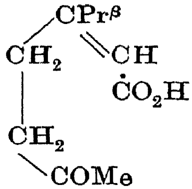
(V.)



(VI.)

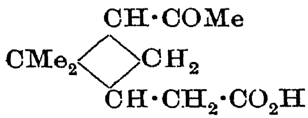


(VII.)

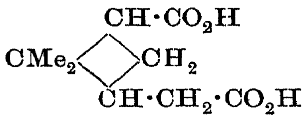


(VIII.)

The instability of pinonic acid (IX), as contrasted with pinic acid (X), can be accounted for on precisely similar lines:



(IX.)



(X.)

This explanation has already been adversely criticised, and it certainly does not appear to be applicable in all cases.[77]

As illustrating the apparent stability in certain cases of the four-carbon ring, as contrasted with that of the three-carbon ring, the case of the condensation of ethyl sodiocyanacetate with ethyl 1-cyano-

[76] D. Thomson, *Trans.*, 1910, **97**, 1502.

[77] G. Cusmano, *Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 63 ; *A.*, i, 686.

*cyclo*butane-1-carboxylate (II) may be cited. Under conditions where the corresponding *cyclo*propane derivative (I) yields an open-chain compound (III), the *cyclo*butane compound is attacked in the side group, yielding the imino-compound (IV)[78]:

$$\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}\!>\!C(CN)\cdot CO_2Et \quad \text{(I.)} \qquad\qquad \begin{matrix} CH_2\cdot C(CN)\cdot CO_2Et \\ | \qquad | \\ CH_2\cdot CH_2 \end{matrix} \quad \text{(II.)}$$

$$\downarrow \qquad\qquad\qquad\qquad \downarrow$$

$$\begin{matrix} CH_2\cdot CH(CN)\cdot CO_2Et \\ | \\ CH_2\cdot CH(CN)\cdot CO_2Et \end{matrix} \quad \text{(III.)} \qquad \begin{matrix} CH_2\cdot C(CO_2Et)\cdot C(NH)\cdot CH(CN)\cdot CO_2Et \\ | \qquad | \\ CH_2\cdot CH_2 \end{matrix} \quad \text{(IV.)}$$

Oxonium and Carbonium Compounds.

Towards the end of last year, and too late for inclusion in the report for 1909, an important paper[79] appeared, in which the view was put forward that a large number of compounds, generally considered as oxonium salts, should be regarded as carbonium compounds. Starting from the hypothesis adopted by Gomberg and Cone[80] to explain the behaviour of triphenylchloromethane and analogous substances, that these compounds are capable of existing in two isomeric modifications, the one aromatic and colourless (I), and the other quinonoid and coloured (II):

(I.) (II.)

these authors assign the "quinocarbonium" structure (II) to a number of derivatives, many of which contain oxygen.

The carboxonium salts, such as those derived from xanthenol, triphenylcarbinol, or benzo-γ-pyranol, are always described as coloured substances. It is shown, however, that the method of isolation is always such that only the quinonoid form would be obtained, even if two modifications were capable of existing. The colourless carbinol dissolves in acids to form a coloured solution, and a coloured ferrichloride may be precipitated, but it cannot be concluded from these facts that the solid carbinol chloride would be coloured. On the contrary, colourless triphenylcarbinol chloride is capable of forming a coloured solution in liquid hydrogen chloride, whilst its colourless methoxyl derivatives yield intensely coloured compounds with hydrochloric acid.

The suspicion, that the colour is only developed in the presence of an excess of acid or of a haloid salt, is confirmed by experiment.

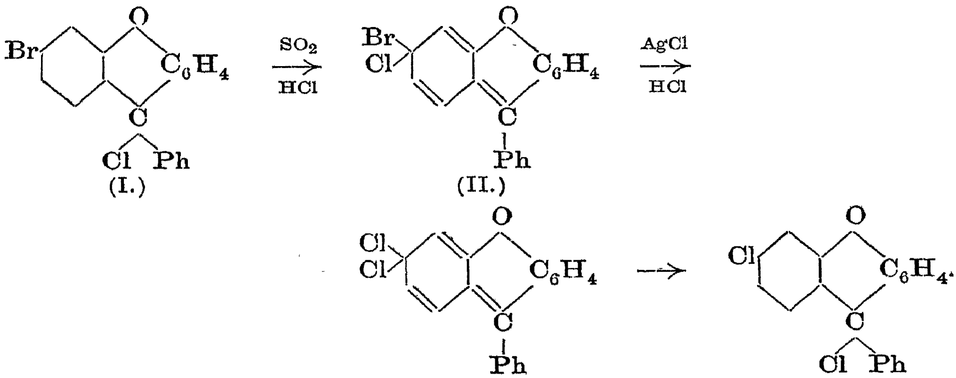
[78] A. F. Campbell and J. F. Thorpe, *Trans.*, 1910, **97**, 2418.

[79] M. Gomberg and L. H. Cone, *Annalen*, 1909, **370**, 142; *A.*, i, 55.

[80] *Ann. Report*, 1907 116.

If xanthenol is dissolved in an indifferent solvent, and hydrogen chloride is passed into the solution, an intensely yellow precipitate is obtained, composed of 1 mol. of xanthenol chloride and 1 mol. of hydrogen chloride. When this hydrochloride is suspended in an indifferent solvent, this mol. of hydrogen chloride may be removed by a current of air, and the resulting xanthenol chloride is colourless. The reactions of these colourless chlorides completely resemble those of the triphenylcarbinol chlorides. Even the preparation of triphenylmethyl finds its parallel in the action of silver on phenylxanthenol chloride, a dark red solution being obtained, which readily absorbs oxygen, precipitating the colourless phenylxanthenol peroxide, $[O<^{C_6H_4}_{C_6H_4}>CPh\cdot]_2O_2$.

Further, the xanthenol chlorides dissolve in liquid sulphur dioxide to coloured solutions, the quinonoid constitution of which is supported by the fact that when the compound taken is the chloride of a *p*-bromo-derivative, it is always possible to recover a bromide of the *p*-chloro-derivative from the solution. Hydrogen chloride is capable of bringing about the same change in benzene solution, whilst the change II ⟶ III is produced even by silver chloride at the ordinary temperature:



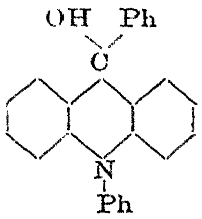
(I.) (II.) (III.) (IV.)

this transformation being exactly similar to that observed in the substituted derivatives of triphenylmethyl chloride.[81]

Complete similarity is observed between the sulphates, double salts, and perchlorates of the xanthenols and of the triphenylmethyl compounds, and as oxygen is absent from the latter, it is considered unnecessary to assume an oxonium structure for the former. The argument is extended to the pyranols, and also to the derivatives of acridine, a very large number of compounds being studied in each class. The case of the acridine compounds is particularly interest-

[81] *Ann. Report*, 1907, 116.

ing. The basic properties of the phenylacridols are generally attributed to the presence of the "bridge" nitrogen. 5 : 10-Diphenylacridol is, however, a derivative of triphenylamine, the basic properties of which are so weak that only two salts, a hydrofluoride and a hydrobromide, the latter existing only at a low temperature, have been isolated. The complete resemblance of 5 : 10-diphenylacridol in its colour reactions, etc., to the xanthenols leads the authors to regard this, and probably all other acridols, as forming quinocarbonium salts.

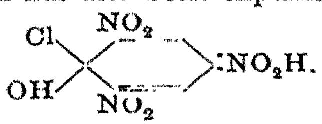


Against this view, Hantzsch[82] has objected that the coloured phenylmethylacridol salts have a high conductivity, comparable with that of the quaternary ammonium salts, and inconsistent with a carbonium structure. The objection has, however, been removed in the meantime by the observation[83] that the dimethyl ether of fluorescein ester, which does not contain nitrogen, yields a chloride, the conductivity of which is of the same order as that of phenylmethylacridol chloride.

In a later paper by Gomberg and Cone,[84] the experiments are extended to thioxanthenols, with similar results, and a number of applications of the quinocarbonium hypothesis are made, in particular the influence of such substituents as hydroxyl and the amino-group being studied. Further, the salts of dimethylpyrone are brought into line with those of the other classes mentioned. It is considered doubtful whether alcohols and phenols ever yield salts with acids in definite stoicheiometric proportions, and the salts of ketones are regarded as being formed by the addition:

$$>C:O + HX = >C<^{OH}_{X}.$$

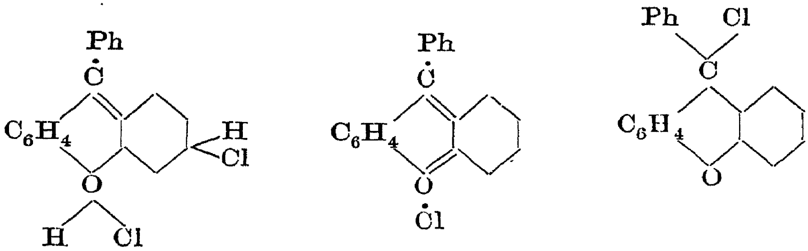
In the same way, dimethylpyrone may be considered to react with acids by virtue of its carbonyl group, addition taking place to form a carbonium salt. The behaviour of picric acid towards hydrogen chloride in solution has also been explained[85] by the formation of a carbonium salt,



The principal opposition to the wide extension proposed to be given to the class of carbonium salts has come from Kehrmann,[86]

[82] *Ber.*, 1910, **43**, 339.
[83] F. Kehrmann, *Annalen*, 1910, **372**, 328 ; *A.*, i, 406.
[84] *Annalen*, 1910, **376**, 183 ; *A.*, i, 869.
[85] A. Stepanoff, *ibid.*, **373**, 219 ; *A.*, i, 471.
[86] F. Kehrmann, *ibid.*, **372**, 287 ; *A.*, i, 406.

who, whilst adopting a quinocarbonium structure in many instances, considers that there is no justification for assuming that all "onium" salts are constituted similarly. The chlorides of phenylxanthenol are formulated thus:



Coloured. Colourless.

As regards the derivatives of acridine, the fact that acridinium salts closely resemble the phenylammonium salts in poisonous properties, taste, etc., is adduced in favour of the attachment of the hydrogen chloride to nitrogen.

A further impetus has been given to the study of carbonium and oxonium compounds by the introduction of a new reagent. This is a concentrated 71 per cent. solution of perchloric acid, which forms highly crystalline, sparingly soluble salts, and has a remarkable capacity for combining with compounds possessing only weak residual affinity.[87] Triphenylmethyl chloride and perchloric acid react at once, hydrogen chloride being liberated. The study of the conductivity of these perchlorates in indifferent solvents gives interesting results.[88] The solution of triphenylmethyl perchlorate in tetrachloroethane is coloured, and conducts electricity, although this solvent is unable to render the corresponding chloride conducting. The solubility in a series of solvents follows the same order as that of mercuric chloride, whilst it is quite different from that of sulphur, thus illustrating the close analogy between carbonium salts and metallic salts, an analogy which is particularly well marked in the dinaphthapyryl salts, $\left(O{<}^{C_{10}H_6}_{C_{10}H_6}{>}CH\cdot\right)X$,[89] which react in solution like the salts of a metal, the sulphide being precipitated by hydrogen sulphide, the picrate by potassium picrate, etc.

Perchloric acid has been utilised in the investigation of a compound formerly[90] obtained from the product of the action of methyl

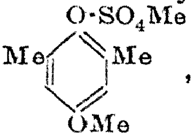
[87] K. A. Hofmann and collaborators, *Ber.*, 1909, **42**, 4856; 1910, **43**, 178, 1080, 2624; *A.*, i, 105, 187, 370, 818.

[88] K. A. Hofmann, H. Kirmreuther, and A. Thal, *ibid.*, 183; *A.*, i, 168.

[89] R. Fosse, *Compt. rend.*, 1909, **148**, 1607; *Bull. Soc. chim.*, 1909, [iv], **5**, 692, 787, 790, 797; *A.*, 1909, i, 599, 666, 667, 734.

[90] F. Kehrmann and A. Duttenhöfer, *Ber.*, 1906, **39**, 1299; *A.*, 1906, i, 447.

sulphate on dimethylpyrone, and then regarded as an oxonium methiodide. The perchlorate reacts with ammonium carbonate to form methoxylutidine, leading to the assumption of the constitution



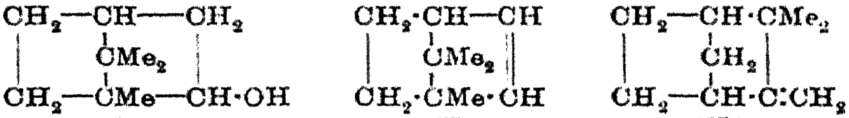
, for the product with methyl sulphate.[91] The alternative carbonium structure is not discussed.

Terpenes and Allied Compounds.

In this section of carbon chemistry, many clear-cut advances have been made during the last few years both by analytic and by synthetic means, but the constitution of camphene, among the less complicated representatives, remains uncertain, and the synthesis of the dimethyl*cyclo*butane complex of pinene and its degradation products has not yet been achieved. The constitution of certain sesqui- and poly-terpenenes, of cholesterol and its relatives, and of caoutchouc, are also outstanding problems to which attention is being devoted.

Camphene and Bornylene.—The isomeric borneols (I), or the corresponding bornyl halides (pinene hydrochloride, etc.), when converted into hydrocarbons by the removal of water or halogen hydride, yield mainly either camphene or bornylene, or both, according to circumstance. Bornylene is known to be the normal product (II), as it yields the same products of oxidation as borneol itself, namely, camphoric acid. The properties of camphene cannot be explained by such a formula, but after long discussion, a way indicated in last year's report, Wagner's formula (III), is now regarded with much favour; C. Harries and J. Palmén[92] have since published the result of their investigations on camphene ozonide, which serve to strengthen the case in its favour.

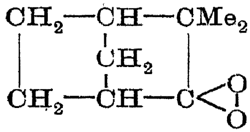
Dimethylnorcampholide, which is certainly represented by (V), appears to be formed by the normal isomeric change of an intermediate perozonide (IV); a transformation of the pinacone pinacolin type is therefore assumed to occur during the formation of camphene from bornyl derivatives:



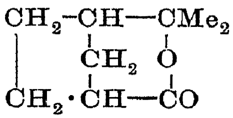
(I.) (II.) (III.)

[91] A. v. Baeyer, *Ber.*, 1910, **43**, 2337; *A.*, i, 763.

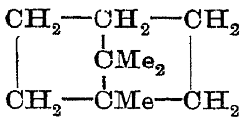
[92] *Ber.*, 1910, **43**, 1432; *A.*, i, 497.



(IV.)



(V.)

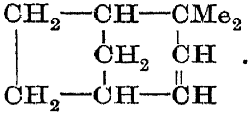


(VI.)

Camphene and bornylene thus contain quite different nuclei, and do not differ, for example, merely in the position of a double linking, and this point has been confirmed in an interesting manner by the comparison of their dihydro-derivatives, which can be obtained by the contact method of reduction devised by Sabatier and Senderens.[93]

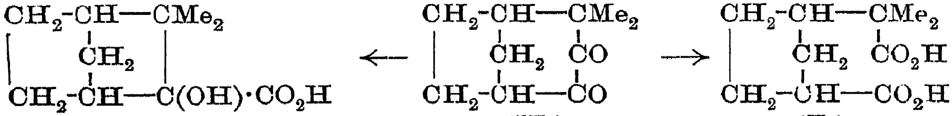
Thus bornylene readily yields camphane (VI), which has already been obtained by Aschan by the reduction of bornyl iodide. Camphene is reduced with more difficulty, and yields a dihydrocamphene which is identical with the substance obtained by Vavon[94] on reducing camphane with hydrogen in presence of platinum-black, and is quite different from camphane.

The evidence in favour of Wagner's formula for camphene is not quite conclusive. Certain important products obtained by oxidising camphene are not readily accounted for by the aid of that structure, but are easily explained by means of (VII), which is closely allied to the former[95]:



(VII.)

Simple oxidation products of (VII) might readily undergo isomeric change of the type associated with the "pinacone" or "benzylic acid" transformations, and yield products derived from the carbon complex of (I); thus the glycol or ozonide from (VII) might become converted into camphenilanaldehyde,[96] and the corresponding diketone (IX) into camphenylic acid (VIII):



(VIII.) (IX.) (X.)

Nearly 70 per cent. of the product obtained by oxidising camphene consists of camphenic acid ("camphenecamphoric acid"), for which the most satisfactory structure is (X). It is certainly an active, saturated dicarboxylic acid, containing only one $>CH{\cdot}CO_2H$ group,

[93] G. G. Henderson and E. F. Pollock, *Trans.*, 1910, **97**, 1620.

[94] G. Vavon, *Compt. rend.*, 1909, **149**, 997; *A.*, i, 52.

[95] O. Aschan, *Annalen*, 1910, **375**, 336; *A.*, i, 709.

[96] Compare *Ann. Report*, 1909, 92.

which may be converted into $>C(OH)\cdot CO_2H$ by the successive actions of bromine and dilute alkali; the resulting hydroxycamphenic acid does not form a lactone, and on fusion with potassium hydroxide yields *iso*butyric, succinic, and oxalic acids.

Wagner considered that the camphenic acid was a secondary product from camphenylic derivatives, but as it is found that the latter cannot be converted into camphenic acid the suggestion appears to have no very sound experimental basis.[97]

Caoutchouc.—The formation of a substance like caoutchouc from isoprene by the action of aqueous hydrochloric acid was noted for the first time by Bourchardat,[98] although Williams,[99] as early as 1860, recorded the fact that isoprene becomes viscid when exposed to air, and spongy products are left when the sticky mass is distilled. Tilden,[1] in 1882, published the results of experiments which confirmed Bourchardat's observation, and drew attention to the fact that the polymerisation also appears to be brought about by the agency of nitrosyl chloride. In 1902, Tilden adduced evidence of the most convincing character that the product obtained from isoprene by slow spontaneous polymerisation has all the properties of the natural rubber; it is only recently, however, that this synthesis of caoutchouc has been acknowledged as a fact beyond dispute, and the substance has now been prepared from isoprene by several methods, although the synthetic article has not appeared on the market among the numerous substitutes for the natural material, for isoprene itself it still something of a chemical curiosity.

Harries found that ozone converted caoutchouc into a di-ozonide, which had the composition and molecular weight corresponding with the formula $C_{10}H_{16}O_6$, indicating that a very substantial dipolymerisation occurs during combination with the agent, the molecule of the product corresponding with only a doubled isoprene molecule. The formula proposed for the ozonide by Harries:

$$O_3<\begin{matrix}CMe\cdot CH_2\cdot CH_2\cdot CH\\ CH-CH_2-CH_2-CMe\end{matrix}>O_3,$$

readily accounted for the lævulinaldehyde obtained from it by treatment with water, and led to Harries' formula for caoutchouc itself, namely:

$$\left(\begin{matrix}CMe\cdot CH_2\cdot CH_2\cdot CH\\ \| \qquad\qquad\qquad \|\\ CH-CH_2-CH_2-CMe\end{matrix}\right)_x.$$

Synthetic rubber from isoprene yields a "tetrabromide" and

[97] O. Aschan, *loc. cit.*
[98] *Compt. rend.*, 1879, **89**, 1117; *A.*, 1880, 323.
[99] *Proc. Roy. Soc.*, 1860, **10**, 517.
[1] *Chem. News*, 1882, **46**, 120; *Brit. Assoc. Report*, 1882; *A.*, 1883, 75.

"nitrosite" apparently identical in all respects with those of the natural hydrocarbon.[2]

Pickles has criticised the formula proposed by Harries, pointing out that the polymerisation of the simple dimethyl*cyclo*octadiene unit conceived by Harries must be either chemical or physical in kind. In the former case, the polymeride would be less unsaturated than the unit, which is not the case, for the bromide contains four bromine atoms for every ten atoms of carbon, but its molecule is still highly complex, perhaps not less so than that of caoutchouc itself. Were Harries' formula correct, it would thus be necessary to suppose that the complex molecule of the tetrabromide is a stable aggregate of saturated molecules:

$$\left(\begin{array}{l}\mathrm{CMeBr\cdot CH_2\cdot CH_2\cdot CHBr}\\ \mathrm{CHBr{-}CH_2\cdot CH_2\cdot CMeBr}\end{array}\right)_x$$

for which no analogy exists. Other reasons are adduced for rejecting Harries' formula, and an alternative one is proposed, in which the caoutchouc molecule is assumed to be constituted as a strictly chemical aggregate of isoprene residues, $(\mathrm{:CMe\cdot CH_2\cdot CH_2\cdot CH:})_x$. This at once accounts for the formation of the bromide and nitrosite with large molecular weights; to explain the formation of the ozonide, the interesting suggestion is made that ozone causes separation of the two doubly linked carbon atoms. The ozonide which results may therefore be formulated as containing, in place of the $>\mathrm{C:C}<$ group of the original caoutchouc, groups of a type which may provisionally be represented as $>\mathrm{C{=}O_3{=}C}<$ in contrast to the type $\underset{\mathrm{O_3}}{>\mathrm{C{-}C}<}$, which is that suggested by Harries.

The state in which caoutchouc exists in the latex of the plants which furnish it has been the subject of some dispute. Weber considered that the fluid contained a hydrocarbon, $C_{20}H_{32}$, from which caoutchouc was formed by a process of polymerisation during the technical preparation of the finished article, whilst de Jong, Tromp de Hass, and Harries held the view that the caoutchouc is present as such in the first instance. A recent determination[3] of the molecular weight, by an indirect process, of the caoutchouc obtained by extracting centrifugalised *Kickxia* milk with benzene, led to the estimated value 3173, which tells seriously against Weber's[4] view as the experimental errors would probably lead to a low rather than a high value.

The same authors have carried out investigations on the nature of the process of vulcanisation of rubber, and infer that the product

[2] S. S. Pickles, *Trans.*, 1910, **97**, 1085.
[3] F. W. Hinrichsen and E. Kindscher, *Ber.*, 1909, **42**, 4329; *A.*, ii, 62.
[4] *Zeitsch. Chem. Ind. Kolloide*, 1910, **6**, 202; *A.*, i, 330.

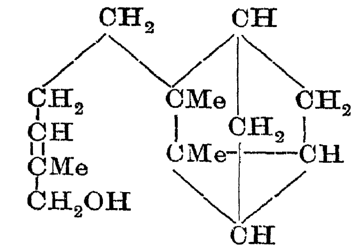
obtained by using sulphur chloride probably contains a definite compound, $(C_{10}H_{16})_2,S_2Cl_2$, and consists of a solution of this substance in caoutchouc with varying quantities of absorbed sulphur.

Attention should be drawn to a useful summary of the numerous researches on cyclic hydrocarbons of the terpene series which contain two double linkings, including those known as terpinenes, which have given rise to so much discussion.[5] All these products appear invariably to be mixtures of isomerides, and the terpinenes proper contain both $\Delta^{1:3}$- and $\Delta^{1:4}$-dihydrocymene, as the oxidation products testify. According to Wallach, the former, or α-terpinene, is identical with Semmler's carvenene, and the latter, or β-terpinene, corresponds with Semmler's *iso*carvenene; but neither of these has been obtained in a pure state.

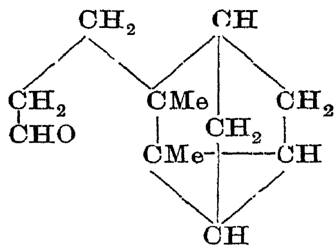
α-Santalol.—Semmler's researches on the sesquiterpene alcohols present in santalol, the oil obtained by distilling sandalwood oil with steam, have been in progress for nearly ten years, and have reached an important stage,[6] inasmuch as certain definite suggestions can be made as to the exact constitution of one constituent. The investigation of other terpenes, with only ten carbon atoms in the molecule, has been notoriously difficult, and it is therefore easy to understand that the study of the structure of similarly constituted substances with molecules containing fifteen carbon atoms calls for extraordinary patience and experimental skill. Santalol contains at least two alcohols, α- and β-santalols; both are probably represented by the molecular formula $C_{15}H_{24}O$, but their complete separation has not yet been effected. Experiments on the various fractions obtained indicated clearly that one of these, α-santalol, is a tricyclic, primary alcohol with an unsaturated linking, and the other, β-santalol, is a bicyclic, primary alcohol, with two double carbon linkings. The fractions of lower boiling point, namely, those richest in α-santalol, yield much tricyclic eksantalic acid, $C_{12}H_{18}O_2$, and the tricyclic aldehyde eksantalol (II), $C_{12}H_{18}O$, with permanganate and ozone respectively. From eksantalol *enol*acetate by oxidation, in the manner indicated in last year's report, noreksantalic acid (III) is produced; the aldehyde corresponding with this again yields an *enol*acetate, which is converted into teresantalic acid. The latter is a saturated dicyclic monocarboxylic acid, and, according to Semmler, may certainly be represented by the formula (IV); if so, there can be little doubt that α-santalol has the constitution (I):

[5] O. Wallach, *Annalen*, 1910, **374**, 217; *A.*, i, 569.

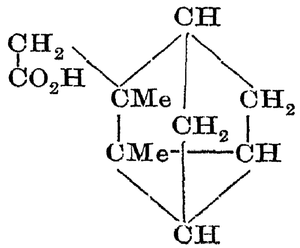
[6] F. W. Semmler, *Ber.*, 1910, **43**, 1722, 1893; F. W. Semmler and B. Zaar, *ibid.*, 1890; *A.*, i, 573.



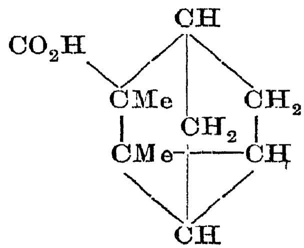
(I.)



(II.)



(III.)



(IV.)

The problem of the relationship between certain rare terpenes has been solved during the course of experiments, which finally led to the complete synthesis of sylvestrene. The ethyl ester of *d*-1-methyl-Δ^1-*cyclo*hexene-3-carboxylic acid (I), obtained by resolution of the inactive acid, was treated with magnesium methyl iodide; the resulting dihydrocarvestrenol (II), which was optically inactive, or nearly so, was converted by hydrochloric acid into the pure dihydrochloride of *d*-carvestrene. This dihydrochloride had $[\alpha]_D + 22{\cdot}0°$, and was identical with sylvestrene dihydrochloride. As the latter compound yields sylvestrene (III) when it is acted on by aniline, the experiments establish the identity of sylvestrene with *d*-carvestrene, and unite in a remarkably concise manner the constitutional and synthetic data which were required to complete this chapter in the history of the terpenes[7]:

$$CH_2{<}\begin{matrix}CMe{:}CH\\CH_2{-}CH_2\end{matrix}{>}CH{\cdot}CO_2H \qquad CH_2{<}\begin{matrix}CMe{:}CH\\CH_2{-}CH_2\end{matrix}{>}CH{\cdot}CMe_2{\cdot}OH$$

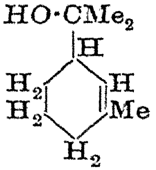
(I.) (II.)

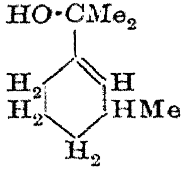
$$CH_2{<}\begin{matrix}CMe{:}CH\\CH_2{-}CH_2\end{matrix}{>}CH{\cdot}CMe{:}CH_2$$

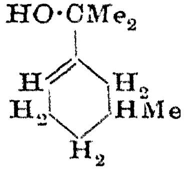
(III.)

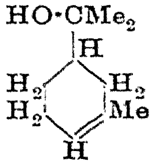
All the six possible menthenols of the meta-series and terpineol type have now been prepared synthetically. These compounds are represented by the structures:

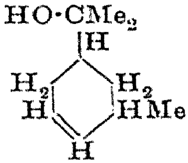
[7] W. H. Perkin, jun., *Proc.*, 1910, **26**, 97.

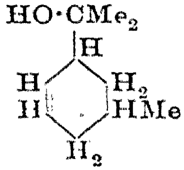

(I.)


(II.)

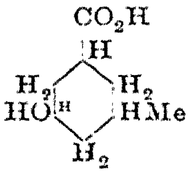

(III.)

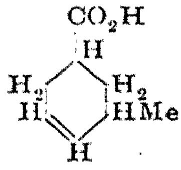

(IV.)

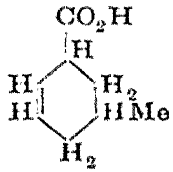

(V.)


(VI.)

The list has been completed during the year 1910 by the addition of (V) and (VI); the starting point for both was 1-methyl*cyclo*-hexane-5-ol-3-carboxylic acid (VII), obtained by the reduction of 5-hydroxy-*m*-toluic acid, from which, by displacement of the hydroxyl group by bromine and removal of the elements of water, the isomeric acids (VIII) and (IX) were obtained and separated:


(VII.)


(VIII.)


(IX.)

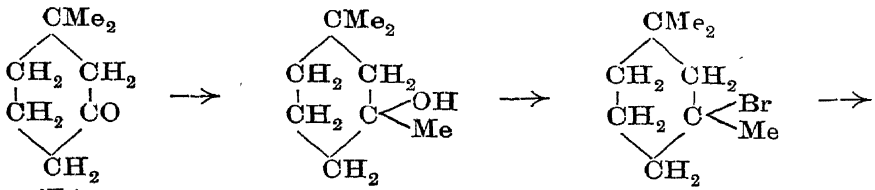
The constitutions of the unsaturated acid were established by identifying the product which they yielded on oxidation, after which their esters were converted into (V) and (VI) respectively by means of magnesium methyl iodide.

The terpenes obtained by dehydrating the menthenols were examined, and possibly represent the corresponding *iso*propenyl-*cyclo*hexenes; it has not yet been found possible to prove that the isomeric *iso*propylidene compounds or terpinolenes are not also formed at the same time.[8]

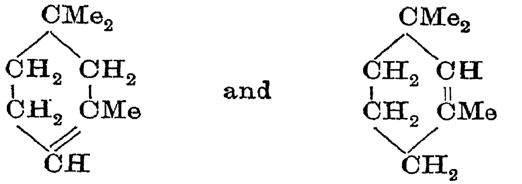
*cyclo*Geraniolene, a mixture of two isomeric 1 : 1 : 3-trimethyl-*cyclo*hexenes (XI) and (XII), obtained originally from citral, has been prepared synthetically from 1 : 1-dimethyl*cyclo*hexan-3-one (X), which is itself a reduction product from synthetic dimethyldihydro-resorcinol.[9] The steps are indicated by the following scheme:

[8] W. H. Perkin, jun., *Trans.*, 1910, **97**, 2129.

[9] A. W. Crossley and C. Gilling, *ibid.*, 2218.

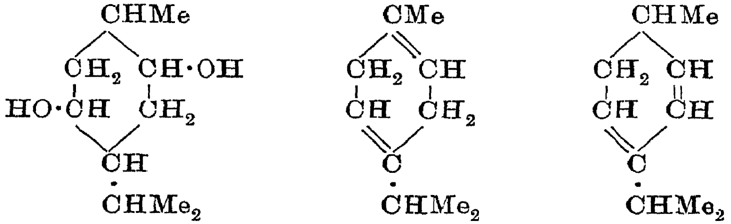


(X.)



(XI.) (XII.)

Among other new syntheses of terpenes may be recorded a simple one from thymoquinol [10]



(I.) (II.) (III.)

On reduction by Sabatier and Senderens' method (compare this report, p. 100), the quinol was converted into menthane-2 : 5-diol, which, on dehydration, gave a terpene, for which the alternative formulæ (II) or (III) are suggested.

Careful comparisons of the properties of certain synthetic terpines and their derivatives from two sources, with those of natural terpineol and limonene derivatives, have been made with the view of eliminating all possible sources of error in the physical constants of these important compounds.[11]

Polyazo-compounds.

Carbon compounds which contain pairs of nitrogen atoms directly united with one another, including diazo- and hydrazo-compounds, hydrazones, and triazens, are now so generally familiar that their division into distinct classes for discussion is probably advantageous, although simple relationships between these and certain ring compounds, such as pyrazoles, may thus conceivably be lost sight of.

Those classes of carbon compounds which contain groups of three

[10] G. G. Henderson and Miss M. M. J. Sutherland, *Trans.*, 1910, **97**, 1616.
[11] W. H. Perkin, jun., and O. Wallach, *ibid.*, 1427.

or more nitrogen atoms directly linked to one another as components of a ring, exhibit certain characteristics and undergo transformations which appear to justify their treatment in a single section.

The most familiar type is doubtless that which includes substances containing the triazo-group, N_3, the residue of diazoimide, and the study of these compounds, initiated by Curtius, has been greatly extended within the last few years, as their great reactivity and the interesting changes which they undergo doubtless accounts for the large amount of attention they have received.

Attempts to prepare triazomalonic ester have so far led to negative results, and the observations made meanwhile indicate that this ester decomposes at the moment of its formation. On the other hand, the triazo-group in mono-alkyl and aryl-malonic esters, $Alk{\cdot}CN_3(CO_2Et)_2$, is remarkably stable, and even resists the action of alkalis, which merely furnish the corresponding substituted triazomalonic acids. Similarly, *α*-triazomethylacetoacetic esters, $Me{\cdot}CO{\cdot}CMeN_3{\cdot}CO_2Et$, may be obtained without extraordinary difficulty, and undergo the normal acetoacetic ester changes with alkalis and acids, yielding triazopropionic acid and triazomethyl ethyl ketone (or, rather, its normal decomposition product, diacetyl).

The observations are explicable in the light of experiments on *α*-triazo-acids, of which only those containing the grouping $>C<^{H}_{N_3}$ undergo the decomposition characteristic of *α*-triazo-ketones, with loss of two-thirds of their nitrogen content. Similarly, the free alkyltriazomalonic acids appear to be attacked by alkalis only in so far as they show some tendency to furnish triazoacetic acids by loss of carbon dioxide; further, the *αα*-bistriazo-derivatives of malonic ester and acetoacetic ester have been isolated, and are found to be moderately stable towards alkalis.[12]

Among the novel and interesting triazo-compounds may be mentioned triazoethylene, $CH_2{:}CH{\cdot}N_3$, a pale mobile liquid, which has been prepared by removing the elements of halogen halide from triazoethyl bromide or iodide, and triazoethyl ether,

$$N_3{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}C_2H_5,$$

which is formed when triazoethyl alcohol reacts with ethyl iodide and silver oxide.[13]

It is now a matter of common knowledge to organic chemists that the triazo-group exhibits a very decided tendency to react with unsaturated atomic groupings and to take part in the formation of new heterocyclic ring systems, such as those of the triazole and

[12] M. O. Forster and R. Müller, *Trans.*, 1910, **97**, 126; M. O. Forster and S. H. Newman, *ibid.*, 1360.

[13] M. O. Forster and S. H. Newman, *ibid.*, 2570.

tetrazole series, this effect being brought about in some cases by internal rearrangement, as with certain unsaturated substances containing the triazo-group, and in other instances by union of different molecular species. During the year some interesting examples have been chronicled.

Methylcarbylamine and anhydrous azoimide unite in ethereal solution, giving rise to a substance, $C_2H_4N_4$, which is considered by its discoverer to be a transformation product of triazomethylenemethylimine (I), and in view of the previous observation of Forster [14] and Schroeter,[15] is probably a derivative of tetrazole (II):

$$N_3H + C{:}NMe \longrightarrow \underset{(I.)}{N_3{\cdot}CH{:}NMe} \longrightarrow \underset{(II.)}{N\!\!<\!\!\begin{array}{l}N{:}CH \\ N{\cdot}NMe\end{array}}$$

Like tetrazole, it is stable towards boiling water, but is decomposed by alkali, yielding carbon dioxide, methylamine, ammonia, and nitrogen.[16]

With fulminic acid (I), azoimide yields a compound which presents all the characters of 1-hydroxytetrazole (III), and probably arises from triazoformoxime (II); its reactions correspond closely with those of Forster's 1-hydroxy-5-phenyltetrazole (*loc. cit.*) [17]:

$$\underset{(I.)}{C{:}NOH} + N_3H \longrightarrow \underset{(II.)}{N_3{\cdot}CH{:}NOH} \longrightarrow \underset{(III.)}{N\!\!<\!\!\begin{array}{l}N{\cdot}N{\cdot}OH \\ N{:}CH\end{array}}$$

Acetylenedicarboxylic acid unites with hydrazoic acid in ethereal solution, yielding 1 : 2 : 3-triazoledicarboxylic acid, and other $\alpha\beta$-acetylenic acids behave in a similar way.[18] Even acetylene reacts with hydrazoic acid in acetone at 100°, and the product is 1 : 2 : 3-triazole (I) itself. Phenylazoimide yields 1-phenyl-1 : 2 : 3-triazole. Tetrazole (II) is the product when hydrogen cyanide and hydrazoic acid are heated together in alcoholic solution [19]:

$$\underset{(I.)}{NH\!\!<\!\!\begin{array}{l}CH{\cdot}CH \\ N{=}N\end{array}} \qquad \underset{(II.)}{NH\!\!<\!\!\begin{array}{l}CH{:}N \\ N{=}N\end{array}}$$

The condensation of phenylazoimide with benzylidenephenyl-

[14] *Trans.*, 1909, **95**, 184.

[15] G. Schroeter, *Ber.*, 1909, **42**, 3356 ; *A.*, 1909, i, 773 ; compare also Thiele, *Annalen*, 1892, **270**, 1 ; *A.*, 1892, 1298 ; and Hantzsch and Vagt, *Annalen*, 1901, **314**, 339 ; *A.*, 1901, i, 194.

[16] E. Oliveri-Mandalà, *Atti R. Accad. Lincei*, 1910, [v], **19**, i, 228 ; *A.*, i, 343.

[17] F. C. Palazzo, *ibid.*, 218 ; *A.*, i, 342.

[18] E. Oliveri-Mandalà and A. Coppola, *ibid.*, 563 ; *A.*, i, 593.

[19] O. Dimroth and G. Fester, *Ber.*, 1910, **43**, 2219 ; *A.*, i, 645.

hydrazone to form 1 : 4-diphenyltetrazole, observed in 1907, is now found to take place in the following manner[20]:

$$CHPh{:}N{\cdot}NHPh + Ph{\cdot}N_3 = \begin{array}{l} C\,Ph{:}N{\cdot}NHPh \\ | \\ N{=\!=}N{\cdot}NHPh \end{array} = \begin{array}{l} C\,Ph{:}N{\cdot}N\,Ph \\ | \qquad\quad | \\ N{=\!=\!=\!=}N \end{array} + Ph{\cdot}NH_2.$$

The conversion of the acylazoimides into carbimides:

$$R{\cdot}CO{\cdot}N_3 = R{\cdot}NCO + N_2,$$

was discovered independently by Schroeter, Forster, and Stoermer. Schroeter was the first to publish any account of such transformations,[21] and the statement to a different effect in last year's report[22] was therefore inaccurate. An interesting reaction, not unattended with danger to the operator, is one in which this transformation plays a part, namely, that which occurs when triazoacetyl chloride is allowed to act on sodium azide. The expected triazoacetylazide, $N_3{\cdot}CH_2{\cdot}CO{\cdot}N_3$, is not observed, but, instead, triazomethylcarbimide is formed:

$$N_3{\cdot}CH_2{\cdot}CO{\cdot}N_3 = N_3{\cdot}CH_2{\cdot}N{:}C{:}O + N_2.$$

This compound very readily loses the triazo-group as hydrazoic acid when in contact with cold solutions of alkali carbonates or with warm water, a property which is in marked contrast with the character of triazoacetic acid, and is considered to be consequent on the presence of nitrogen directly attached to the carbon atom on which the triazo-group is situated.

The carbimide is readily converted into a compound which is almost certainly tristriazomethyl *iso*cyanurate, $(N_3{\cdot}CH_2{\cdot}NCO)_3$, since it is resolved by weak alkali into cyanuric acid, hydrazoic acid, and formaldehyde:

$$(N_3{\cdot}CH_2{\cdot}NCO)_3 + 3H_2O = 3N_3H + (HNCO)_3 + 3CH_2{:}O.$$

Derivatives of the carbimide, such as those obtained by the action of ammonia and water, furnish formaldehyde by alkaline hydrolysis, the replacement of $\cdot N_3$ by $\cdot OH$ doubtless leading to the formation of derivatives of formaldehyde-ammonia at the intermediate stage:

$$N_3{\cdot}CH_2{\cdot}NHX \longrightarrow HO{\cdot}CH_2{\cdot}NHX \longrightarrow CH_2{:}O + NH_2X.$$[23]

The analogy which subsists between derivatives of 1 : 2 : 3-triazole and diazoamino-compounds was referred to in a former report.[24] In both series is present the grouping $\cdot NR{\cdot}N{:}N\cdot$, and the transformations which the 5-aminotriazoles undergo suggest that the three-membered nitrogen chain may be resolved in the same manner as that in diazoamino-compounds, furnishing an amino-residue and

[20] O. Dimroth and S. Merzbacher, *Ber.*, 1910, **43**, 2899 ; *A.*, i, 897.
[21] *Chem. Zeit.*, 1908, **32**, 933.
[22] *Ann. Report*, 1909, 71 ; compare M. O. Forster and R. Müller, *Trans.*, 1910, **97**, 1057.
[23] M. O. Forster and R. Müller, *Trans.*, 1910, **97**, 1056.
[24] *Ann. Report*, 1909, 72.

a diazo-residue. These considerations have led to a revision of former views as to the nature of the isomeric changes which occur when certain substituted 5-hydroxy-1 : 2 : 3-triazoles (I) are fused or dissolved in organic solvents. It was formerly supposed that the relation between the isomerides was dependent on keto-enolic isomerism, and the alternative structure (II) for the neutral isomerides had been rejected because it represented them as derivatives of diazo-anhydrides, a supposition which appeared to be

$$\mathrm{NR}<\begin{matrix}\mathrm{C(OH)}\\ \mathrm{N{=}N}\end{matrix}>\mathrm{CR'} \qquad\qquad \mathrm{O}<\begin{matrix}\mathrm{C(NHR)}\\ \mathrm{N{=}N}\end{matrix}>\mathrm{CR'}$$

(I.) (II.)

inconsistent with their remarkable stability.

On the other hand, a complex similar to (II) was assumed by Piloty and Neresheimer to be present in ethyl diazomalonate, because this substance is not prone to decomposition, but the necessity for such a conclusion disappears when the properties of diazomethane and diazoacetic acid are contrasted, for a great fall in reactivity consequent on the displacement of a hydrogen atom by a carbethoxy-group is then revealed. Ethyl diazomalonate, by the action of cold aqueous ammonia, is converted into ethyl diazomalonamate (III), and the latter, in presence of sodium ethoxide, undergoes conversion into ethyl 5-hydroxy-1 : 2 : 3-triazole-4-carboxylate, which on fusion regenerates ethyl diazomalonamate.

$$\begin{matrix}\mathrm{N}\\ \|\\ \mathrm{N}\end{matrix}>\mathrm{C}<\begin{matrix}\mathrm{CO{\cdot}NH_2}\\ \mathrm{CO_2Et}\end{matrix} \quad \underset{\text{fusion}}{\overset{\text{NaOEt}}{\rightleftarrows}} \quad \mathrm{N}<\begin{matrix}\mathrm{C(OH)}\\ \mathrm{N{=}N}\end{matrix}>\mathrm{C{\cdot}CO_2Et}$$

(III.) (IV.)

These facts are not in harmony with the views of Piloty and Neresheimer, and a formula corresponding with (III) must be adopted for diazomalonic ester.

The constitution of the neutral isomerides (VI) of the 5-hydroxy-triazoles follows readily if this conclusion be accepted. The former are yellow, whilst the hydroxytriazoles are colourless. The substance having the formula (VII) (formerly supposed to be methyl 1-phenyl-5-triazolone-4-carboxylate) can be converted by alcoholic hydrogen sulphide into a hydrazi-compound (VIII), similar in all important characters to ethyl hydrazimalonate, and yielding hydrazine with hydrochloric acid:

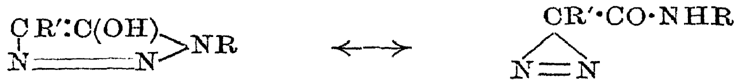
$$\mathrm{NHR{\cdot}CO{\cdot}CR'}<\begin{matrix}\mathrm{N}\\ \|\\ \mathrm{N}\end{matrix} \qquad\qquad \mathrm{NHPh{\cdot}CO{\cdot}C(CO_2Me)}<\begin{matrix}\mathrm{N}\\ \|\\ \mathrm{N}\end{matrix}$$

(VI.) (VII.)

$$\mathrm{NHPh{\cdot}CO{\cdot}C(CO_2Me)}<\begin{matrix}\mathrm{NH}\\ |\\ \mathrm{NH}\end{matrix}$$

(VIII.)

It thus appears that the hydroxy-triazoles in question and diazo-amides are usually mutually intraconvertible, as indicated by the scheme:



The formation of the diazo-compounds from the triazoles is not to be observed in all cases; for example, 5-hydroxytriazole itself is stable; the reverse change, however, which is brought about by alkalis, seems to be general and complete.[25]

Diazo-compounds.—Whilst the question of the constitution of the aromatic diazo-compounds has received little attention during the past year, several interesting investigations have dealt with this class. The isolation of azomethane in 1909 [26] renewed the hope of obtaining diazo-compounds, similar to those of the aromatic series, but containing purely aliphatic radicles. The compound obtained by Thiele in 1892, and then supposed to be diazoguanidine nitrate, was shown by Hantzsch [27] to be carbaminoiminoazoimide nitrate, $NH:C(NH_2)\cdot N_3,HNO_3$. By diazotising aminoguanidine dinitrate at 0° in neutral solution, however, aminoguanidine diazohydroxide, $C_2H_7N_{10}\cdot OH$,[28] which behaves like an aromatic diazohydroxide, forming salts which couple with aromatic amines, and losing nitrogen when boiled with water, is obtained. The amphoteric character of the hydroxide, which forms crystalline salts with metals as well as with acids, proves that it is not a diazonium compound, and its reactions indicate that it contains either the *anti*-diazohydroxide group, $\cdot NH\cdot N:N\cdot OH$, or the nitrosoamine group, $\cdot NH\cdot NH\cdot NO$.[29] The two carbon atoms are connected by the tetrazen group, thus:

$$\begin{matrix}NH\\NH_2\end{matrix}\!\!>C\cdot NH\cdot NH\cdot N:N\cdot C\!<\!\!\begin{matrix}NH\\N_3H_2O\cdot\end{matrix}$$

It has been proved that the tetrazole ring is absent.

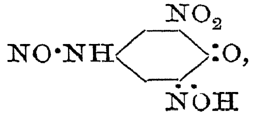
The product obtained by the action of nitrous acid on aminoguanidine dinitrate in acetic acid is a diazoamino-derivative of tetrazole, $\begin{matrix}HN\cdot N\\ N:N\end{matrix}\!\!>C\cdot N:N\cdot NH\cdot C\!<\!\!\begin{matrix}N\cdot NH\\ N:N\end{matrix}$,[30] and has strongly acid properties.

The tendency of recent work on these and other diazotisable compounds is to show that a close analogy exists in this respect between aromatic compounds and open-chain compounds in which

[25] O. Dimroth, *Annalen*, 1910, **373**, 336; *A.*, i, 518.
[26] *Ann. Report*, 1909, 95.
[27] A. Hantzsch and A. Vagt, *Annalen*, 1901, **314**, 339; *A.*, 1901, i, 194.
[28] K. A. Hofmann and R. Roth, *Ber.*, 1910, **43**, 682; *A.*, i, 232.
[29] K. A. Hofmann, H. Hock, and R. Roth, *ibid.*, 1087; *A.*, i, 446.
[30] K. A. Hofmann and H. Hock, *ibid.*, 1866; *A.*, i, 547.

there is a certain distribution of groups possessing residual affinity, and the possibility still remains that true diazonium compounds may be obtained in the aliphatic series, given a suitable distribution of unsaturated linkings.

Amino-derivatives of triazole are known to be diazotisable, and the stability of the resulting compound is particularly great in the case of the carboxylic acid, the product resembling diazobenzoic acid, although containing the elements of an additional molecule of water. The sparing solubility and great stability are evidently due to the influence of the heavy carboxyl group, as it is found[31] that phenyl confers similar properties, phenyltriazole diazohydroxide, $\begin{matrix} N-NH \\ \| \\ CPh\cdot N \end{matrix} > C\cdot N_2\cdot OH$, being comparatively stable. In this case, as with the corresponding derivatives of guanidine and thiazole, it is uncertain whether the compound should be regarded as an *anti*-diazohydroxide or as a nitrosoamine. A stable primary nitrosoamine may be prepared by the action of nitrous acid on 6-nitro-4-amino-resorcinol, when a derivative of *o*-benzoquinoneoxime,



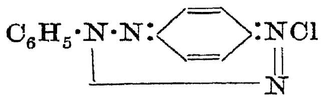
is obtained.[32] The *anti*-diazohydroxide constitution in this case is excluded by the absence of any reaction with acetyl chloride, and by the failure to couple with alkaline β-naphthol when a solution of the nitrosoamine in alcoholic hydrogen chloride is used, although the normal diazonium salt, obtained by the action of fuming hydrochloric acid, couples readily.

The remarkable stability conferred on aromatic diazonium salts by the introduction of heavy radicles has been previously noticed.[33] It is now found[34] that the naphthalene derivatives, which contain a labile hydrogen atom that might possibly migrate, giving rise to a quinonoid compound, retain their remarkable properties, including their deep colour, when this hydrogen is replaced by ethyl, as in $N_2X\cdot C_{10}H_6\cdot NEt\cdot CO\cdot C_6H_5$. The same observation had been made previously in the benzidine series, and the proof is now complete for a series of *p*-benzoylaminoaryl- or *p*-benzoylalkylamino-aryl-diazonium salts, all of which exhibit considerable stability, whilst the colour increases with the complexity of the aryl group, the benzene series being colourless, the diphenyl series coloured to a

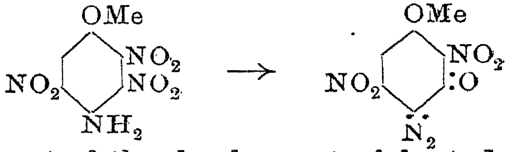
[31] W. Manchot, *Ber.*, 1910, **43**, 1312; *A.*, i, 442.
[32] G. Heller and A. Sourlis, *ibid.*, 2581; *A.*, i, 749.
[33] *Ann. Report*, 1907, 120.
[34] G. T. Morgan and E. G. Couzens, *Trans.*, 1910, **97**, 1691.

varying extent, and the naphthalene series uniformly coloured. The evidence is decisive against the assumption of different structures for coloured and colourless diazonium salts.

Another stable diazonium salt has been observed in benzeneazobenzenediazonium chloride, the absorption spectrum of which greatly resembles that of benzeneazophenyltrimethylammonium iodide,[35] and a quinonoid diazonium formula is suggested:

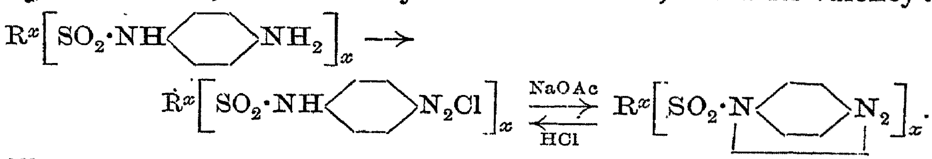


A further instance of the elimination of a nitro-group during diazotisation has been observed in 2 : 3 : 5- and 2 : 3 : 6-trinitro-*p*-anisidines, the 3-nitro-group of which is eliminated, yielding a quinonediazide[36]:



The measurement of the development of heat during the diazotisation of amines and the coupling of the resulting compounds with phenols has been employed[37] as a means of studying these reactions. One of the conclusions arrived at is that the conversion of a diazonium hydroxide, $\begin{matrix} R\cdot N\cdot OH \\ \vdots \\ N \end{matrix}$, into a diazohydroxide, R·N:N·OH, is accompanied by little or no heat change.

The conversion of a diazonium salt into a diazohydroxide is probably the intermediate stage in the formation of diazoimides, a reaction that has been studied in the case of sulphonyl derivatives.[38] In the following scheme, R may represent either an alkyl, aromatic, hydro-aromatic, or mixed alkyl-aromatic radicle, and x its valency:



The reversible change probably takes place in several stages. In presence of sodium acetate, the diazonium chloride is converted into an acetate, which then undergoes hydrolysis to a greater or less extent, and the resulting diazohydroxide then undergoes internal

[35] J. T. Hewitt and F. B. Thole, *Trans.*, 1910, **97**, 511.
[36] R. Meldola and F. Reverdin, *ibid.*, 1204.
[37] W. Sventoslavsky, *Ber.*, 1910, **43**, 1479, 1488, 1767 ; *A.*, ii, 588.
[38] G. T. Morgan and J. A. Pickard, *Trans.*, 1910, **97**, 48.

condensation. When the radicle R is a heavy one, the insoluble diazoimide is precipitated, but the simplest members of the class, such as $CH_3{\cdot}SO_2{\cdot}\overline{N{\cdot}C_6H_4{\cdot}N_2}$, remain dissolved in a hydrated form, and are only isolated by evaporation. These *p*-diazoimides are always coloured substances, whilst their ortho-analogues are colourless, and the proper formulation of the compounds of this class thus becomes of interest. Two formulæ, (I) and (II), have been suggested for the cyclic diazoimines and diazoimides by Griess and Kekulé respectively:

$$C_6H_4{<}\begin{matrix}N\\|\\N\end{matrix}{>}NR \qquad\qquad C_6H_4{<}\begin{matrix}N\\NR\end{matrix}{>}N$$

(I.) (II.)

where R is a hydrogen atom or an alkyl, aryl, or acyl group. A decision between the two formulæ is made possible by the introduction of a substituent into the benzene ring in order to render the molecule less symmetrical.[39] Representing the substituent by X, two isomerides are possible if Kekulé's formula is correct, namely, $C_6H_3X{<}\begin{matrix}N_2\\|\\NR\end{matrix}$ and $C_6H_3X{<}\begin{matrix}NR\\|\\N_2\end{matrix}$, whilst only one product would be obtained if the structure were represented by Griess's formula. Instead of introducing a substituent, *o*-naphthylene compounds may be used in place of their *o*-phenylene analogues. The experimental results are in accordance with the first of these alternatives, two isomerides being obtained in each case when the compounds studied were the *o*-naphthylenediamines and their benzenesulphonyl derivatives. All these ortho-compounds are colourless, and are not hydrolysed by concentrated acids, whilst their para- and peri-isomerides are yellow, and are decomposed by acids. As the former compounds contain a five-membered triazole ring, and the latter a seven- and six-membered triazole ring respectively, the colour and instability of the compounds containing the larger number of atoms in the ring is attributed to the strain thereby introduced.

Constitution of iso*Nitroamines.*—*iso*Nitroamines (substituted nitrosohydroxylamines) form two types of esters, for which the constitutions (I) and (II) have been suggested:

$$NO{\cdot}NR{\cdot}OR' \qquad\qquad R{\cdot}NO{:}N{\cdot}OR' \text{ or } R{\cdot}\underset{\underset{O}{\vee}}{N{\cdot}N}{\cdot}OR'$$

(I.) (II.)

The former, on decomposition, readily yield nitrous acid, whilst the latter are stable or else give off nitrous oxide.

[39] G. T. Morgan and W. Godden, *Trans.*, 1910, 97, 1702.

Similarly, the nitroamines give two series of esters supposed to be representable by the formulæ (III) and (IV):

$$NO_2\cdot NRR' \qquad\qquad R\cdot N{:}NO\cdot OR' \text{ or } R\cdot\underset{\diagdown\,O\,\diagup}{N\cdot N}\cdot OR'$$

(III.) (IV.)

and these substances decompose in much the same way as do (I) and (II) respectively. Therefore those esters which are not true nitro- or nitroso-compounds lose the whole of their nitrogen of their characteristic complex, whilst the isomeric ones do not.

In the case of the pure *iso*nitroamines, decomposition occurs as a rule in accordance with only one of these modes, and hence it may be surmised that they correspond in some cases with the type (I), in other cases with type (II).

Menthone*iso*nitroamine (V), however, can be decomposed in both ways; for example, when heated, it yields both pulegone (VII) and β-nitromenthone (VI) (the latter being formed from nitrosomenthone by a secondary process of oxidation). On the other hand, in presence of alkali, only pulegone and nitrous oxide are obtained.[40]

$$CHMe{<}{CH_2\text{—}CO \atop CH_2\cdot CH_2}{>}CH\cdot CMe_2\cdot N(NO)\cdot OH \text{ or }$$

$$CHMe{<}{CH_2\text{—}CO \atop CH_2\cdot CH_2}{>}CH\cdot CMe_2\cdot N_2O\cdot OH$$

(V.)

$$CHMe{<}{CH_2\text{—}CO \atop CH_2\cdot CH_2}{>}CH\cdot CMe_2\cdot NO_2 \qquad CHMe{<}{CH_2\text{—}CO \atop CH_2\cdot CH_2}{>}C{:}CMe_2$$

(VI.) (VII.)

A similar behaviour is exhibited by α-pinenenitrohydroxylamine-oxime.[41]

Triazens.—The first representative of the class of simple mono-substituted triazens, phenyltriazen, $C_6H_5\cdot N{:}N\cdot NH_2$, was prepared in 1907,[42] and was then found to exist in two isomeric forms. The products obtained on reducing substituted phenylazoimides are even less stable than phenyltriazen itself in many instances, but the *p*-bromo-, *p*-benzoyl, and *p*-carbethoxy-derivatives are somewhat more stable,[43] and the first is capable of undergoing an isomeric rearrangement, which the instability of all such derivatives towards reagents does not allow to be further investigated. Benzylazoimide yields only benzylamine and nitrogen on reduction, and so far an aliphatic mono-substituted triazen has not been prepared. On reducing hydrazoic acid with a copper-zinc couple at a sufficiently

40 G. Cusmano, *Gazzetta*, 1909, **39**, ii, 453; *A.*, i, 182.
41 G. Cusmano, *Atti R. Accad. Lincei*, 1910, [v], **19**, i, 747; *A.*, i, 574.
42 O. Dimroth, *Ber.*, 1907, **40**, 2376; *A.*, 1907, i, 653.
43 O. Dimroth and K. Pfister, *ibid.*, 1910, **43**, 2757; *A.*, i, 904.

low temperature, a solution is obtained which appears to contain triazen, $NH{:}N\cdot NH_2$, although decomposition proceeds very rapidly. Further lowering of the temperature merely prevents reduction, and we are therefore still without knowledge of the parent substance of the triazen series.

Mixed aliphatic aromatic triazens, like their purely aromatic analogues, exhibit dynamic isomerism, and the study of compounds of this series, in which the aliphatic group is of high molecular weight, has marked advantages when it is desired to investigate the course followed by the reaction. Methylaminocamphor reacts with diazonium salts, and the resulting camphorylphenylmethyltriazen must have the constitution $C_8H_{14}<\begin{matrix}CH\cdot NMe\cdot N{:}N\cdot C_6H_5\\ |\quad\quad\quad\quad\quad\quad\quad\\ CO\quad\quad\quad\quad\quad\quad\quad\end{matrix}$, since acids resolve its salts into methylaminocamphor and the original diazonium salt.[44] Camphorylphenyltriazen, on the other hand, is unstable towards acids, nitrogen being liberated. This behaviour, coupled with the reaction with phenylcarbimide, which forms camphordiazodiphenylcarbamide, suggests that the triazen has the constitution (I) rather than (II):

$$C_8H_{14}<\begin{matrix}CH\cdot N{:}N\cdot NH\cdot C_6H_5\\ |\quad\quad\quad\quad\quad\quad\quad\\ CO\quad\quad\quad\quad\quad\quad\quad\end{matrix} \qquad\qquad C_8H_{14}<\begin{matrix}CH\cdot NH\cdot N{:}N\cdot C_6H_5\\ |\quad\quad\quad\quad\quad\quad\quad\\ CO\quad\quad\quad\quad\quad\quad\quad\end{matrix}.$$

(I.) (II.)

In previous investigations of the aliphatic-aromatic triazens,[45] whilst the action of acids has followed the course indicated by formula (I), the molecule being resolved into the arylamine, nitrogen, and alkyl chloride by hydrogen chloride, the action of phenylcarbimide has been to convert them into a carbamide, from which acids liberate the aryldiazonium salt. Forster and Garland consider, however, that the formula (I) is to be preferred for all such mixed triazens, and that the anomalous behaviour with phenylcarbimide is to be attributed to the isomerisation of the resulting carbamide. Whilst this isomeric transformation generally proceeds too rapidly for any intermediate compound to have been as yet detected, the weighting of the molecule by the heavy camphor residue retards it considerably, and the first product (III) is readily isolated, being transformed quantitatively into (IV) when the solution in pyridine is heated or exposed to light:

$$C_8H_{14}<\begin{matrix}CH\cdot N{:}N\cdot N\cdot C_6H_5\quad\quad\\ |\quad\quad\quad\quad\quad |\quad\quad\quad\quad\\ CO\quad\quad\quad\quad CO\cdot NH\cdot C_6H_5\end{matrix} \longrightarrow C_8H_{14}<\begin{matrix}CH\cdot N\cdot N{:}N\cdot C_6H_5\\ |\quad\quad |\quad\quad\quad\quad\quad\\ CO\ \ CO\cdot NH\cdot C_6H_5\end{matrix},$$

(III.) (IV.)

and although such a reaction involves the migration of so heavy a group as $C_6H_5\cdot NH\cdot CO\cdot$, it affords the most satisfactory explanation

[44] M. O. Forster and C. S. Garland, *Trans.*, 1909, **95**, 2051.

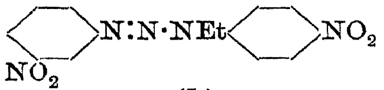
[45] O. Dimroth, *Ber.*, 1905, **38**, 670 ; *A.*, 1905, i, 311.

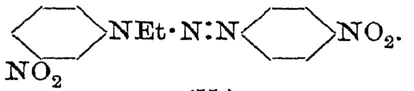
of the facts. The authors review the evidence, mainly due to Dimroth, for the alternative formula for the triazens, and conclude that it is not in opposition to their conclusions. The formation of the mixed triazens from an aryldiazonium salt and an aliphatic primary amine has then to be attributed to the attraction exerted by the aryl group on the hydrogen atom being sufficient to bring about the change:

$$\text{Alk}\cdot\text{NH}\cdot\text{N:N}\cdot\text{Ar} \longrightarrow \text{Alk}\cdot\text{N:N}\cdot\text{NH}\cdot\text{Ar}.$$

The principle is extended to the aromatic triazens containing two different aryl groups, and the transformation recorded above, taken in conjunction with existing evidence, renders suspect conclusions as to structure derived from a study of the action of phenylcarbimide, once a favourite reagent for the purpose, and employed very largely by Goldschmidt and others in work on the triazens.

The question of the constitution of triazens containing two different aromatic radicles has also been approached in another manner. In the very extensive series of investigations by Meldola and Streatfeild in 1886–1895, it was demonstrated that three isomeric alkylated diazoamino-compounds could be obtained. Thus, whilst diazotised *m*-nitroaniline and *p*-nitroethylaniline yield the compound (I), diazotised *p*-nitroaniline and *m*-nitroethylaniline yield the compound (II), the third isomeride, obtained by the direct ethylation of *mp′*-dinitrodiazoaminobenzene, being regarded as a compound of (I) and (II):


(I.)


(II.)

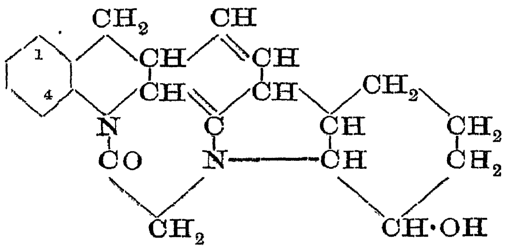
It is now found [46] that the absorption spectra of (I) and (II), although similar, present quantitative differences, whilst (III) has a spectrum intermediate in character between those of (I) and (II), and identical with that of the non-ethylated triazen. The melting-point curve of mixtures of (I) and (II) is a continuous one with a minimum, indicating that the isomeride (III) is an equilibrium mixture of (I) and (II), and not a compound. Unfortunately, the melting points were determined instead of the freezing points, and the resulting curve therefore does not indicate whether the minimum is due to a solid solution or to a eutectic mixture of the two components, but the conclusion, that the product (III) is an equilibrium mixture of (I) and (II), is now well established for the case investigated. If the non-ethylated triazens are also regarded as equilibrium mixtures, then the formation of only a single product by the action of, for instance, phenylcarbimide, must be attributed

[46] C. Smith and Miss C. H. Watts, *Trans.*, 1910, **97**, 562.

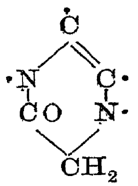
to a selective attack of the reagent, equilibrium being continually restored by the conversion of the one isomeride into the other. When, however, the aryl groups differ widely in character, instead of being very similar, as in the case examined, it is possible that the triazen may consist entirely of one or other of the possible isomerides, this having been shown to occur in the parallel instance of the amidines, ArN:CPh·NHAr'.[47] The physico-chemical methods referred to above are likely to afford useful information in cases of this kind.

Alkaloids.

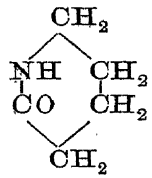
Steady progress has been made in determining the structure of several of the more complex alkaloids, but investigations in this group involve so many experimental stages, and the structures are in general so elaborate, that space does not permit of more than a bare summary of the results obtained. First in general interest stands a systematic review of the evidence for the constitution of the important alkaloids, strychnine and brucine.[48] The mode of union of the quinoline and carbazole nuclei in the strychnine molecule is discussed, and the annexed formula is arrived at as representing the chemical properties of strychnine most completely. Brucine differs from strychnine only in the presence of methoxy-groups as substituents in positions 1 and 4.



The poisonous properties of the two alkaloids are to be attributed to the ring containing the two nitrogen atoms (I), as α-piperidone (II) is found to have very similar properties:



(I.)



(II.)

The presence of a double linking in one of the rings is also shown by the formation of a dibromide[49] and of a peroxide containing

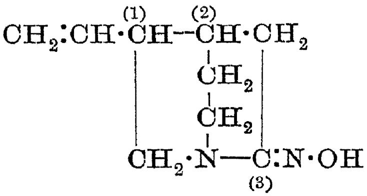
[47] H. v. Pechmann, *Ber.*, 1895, **28**, 869; *A.*, 1895, i, 347.

[48] W. H. Perkin, jun., and R. Robinson, *Trans.*, 1910, **97**, 305.

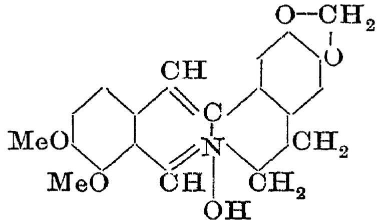
[49] R. Ciusa and G. Scagliarini, *Atti R. Accad. Lincei*, 1910, [v], **19**, i, 555; *A.*, i, 583.

two atoms of active oxygen.[50] Other reactions which have been studied[51] are also consistent with the above interpretation.

The configurations of the cinchona alkaloids have been discussed afresh, in view of the fact that quinine, quinidine, cinchonine, and cinchonidine all yield the same α-oximino-β'-vinylquinuclidine (I) when the ketones obtained from them by oxidation react with amyl nitrite, showing that all these alkaloids have the same spacial configuration with regard to the asymmetric atoms (1) and (2), whilst the properties of the deoxy-bases prove that the isomerism of quinine and quinidine, and also of cinchonine and cinchonidine, depends on the mirror-image arrangement of the substituents around the carbon atom (3)[52]:



(I.)



(II.)

A revision of the reactions of berberine[53] shows that the methoxy-groups have hitherto been wrongly placed, and the formula (II) is proposed. The fact that α-phenyldihydroberberine yields small quantities of 2-benzoyl-3 : 4-dimethoxybenzoic acid on oxidation with permanganate is held[54] to support Perkin's formula (II).

Since tetrahydroberberine contains an asymmetric carbon atom, the addition of an alkyl iodide should produce two isomeric iodides, and this is found to be the case.[55]

A method for the preparation of 1-substituted *iso*quinoline bases consists in the condensation of acylated carbinols of the form $OH \cdot CHPh \cdot CH_2 \cdot NH \cdot CO \cdot R$ (in which R = Me, Ph, or benzyl) with phosphoric acid and xylene, and this may be found useful in the synthesis of alkaloids belonging to this group.[56]

[50] G. Mossler, *Monatsh.*, 1910, **31**, 329 ; *A.*, i, 584.

[51] H. Leuchs and P. Boll, *Ber.*, 1910, **43**, 2362 ; H. Leuchs and P. Reich, *ibid.*, 2417 ; *A.*, i, 766, 767.

[52] P. Rabe, *Annalen*, 1910, **373**, 85 ; *A.*, i, 417.

[53] Perkin and Robinson, *loc. cit.*

[54] F. Faltis, *Monatsh.*, 1910, **31**, 557 ; *A.*, i, 698.

[55] A. Voss and J. Gadamer, *Arch. Pharm.*, 1910, **248**, 43 ; *A.*, i, 415.

[56] A. Pictet and A. Gams, *Ber.*, 1910, **43**, 2384 ; *A.*, i, 773.

The name "pavine" is proposed[57] for the compound formerly described by Goldschmiedt as tetrahydropapaverine and by Pyman as 1 : 2-dihydropapaverine, the constitution of which is still somewhat doubtful. The relationship of pavine to laudanosine is represented by the following scheme:

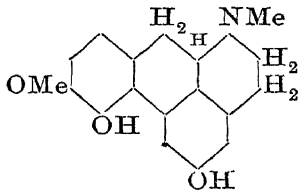
Papaverine methosulphate $\xrightarrow{+2H_2}$ Laudanosine

$+H_2$ ↘ ↙ $-H_2$

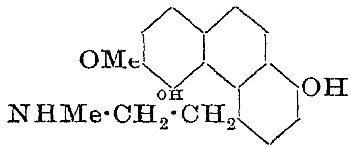
N-Methylpavine.

The alkaloid cryptopine, which commonly accompanies papaverine, is found to be a saturated base, and to contain two methoxy-groups and one methyl attached to nitrogen. There is no phenolic, alcoholic, or ketonic oxygen.[58]

In the morphine series, the production of pyrene when thebaine is distilled with zinc dust, affirmed in 1897 but denied by later workers, is now confirmed.[59] Other work on this group relates to the ethylthiocodides and ethylthiomorphides.[60] The constitutions (I) and (II) are assigned to morphothebaine and thebenine, on the ground of the formation of 1 : 3 : 5 : 6-tetramethoxyphenanthrene from the former, and of 3 : 4 : 8-trimethoxyphenanthrene from the latter[61]:



(I.)



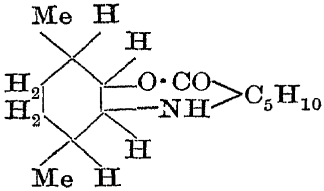
(II.)

The synthesis of narcotine is now completed by the synthesis of cotarnine from myristicin, a tabular statement of the steps involved being given.[62] Gnoscopine is found to be the racemic form of narcotine. It is not present in poppy-juice, but is formed by racemisation during extraction.[63]

Other work relates to picrotin and picrotoxin, some of the

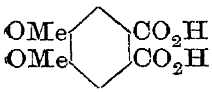
[57] F. L. Pyman and W. C. Reynolds, *Trans.*, 1910, **97**, 1320.
[58] A. Pictet and G. H. Kramers, *Ber.*, 1910, **43**, 1329 ; *A.*, i, 502.
[59] M. Freund, *ibid.*, 2128 ; *A.*, i, 631.
[60] R. Pschorr and A. Rollett, *Annalen*, 1910, **373**, 1 ; R. Pschorr, *ibid.*, 15, 45 ; *A.*, i, 419, 421, 423.
[61] R. Pschorr, *ibid.*, 51 ; R. Pschorr and F. Zeidler, *ibid.*, 75 ; *A.*, i, 423, 425.
[62] A. H. Salway, *Trans.*, 1910, **97**, 1209.
[63] P. Rabe and A. McMillan, *Ber.*, 1910, **43**, 800 ; *A.*, i, 335.

reactions of which have been studied,[64] and to carpaine, to which the formula:

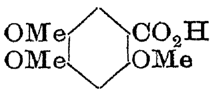


is provisionally assigned, the nature of the group C_5H_{10} being unknown.[65]

The synthesis has also been effected of two compounds, which are of importance on account of their occurrence as degradation products of alkaloids. These are *m*-hemipinic (I) and asaronic (II) acids:



(I.)



(II.)

(III.)

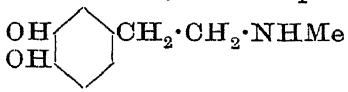
The former is obtained from creosol (III) by methylation, nitration, reduction, and conversion into the nitrile, followed by hydrolysis and oxidation with alkaline permanganate. Asaronic acid is prepared by oxidising the dimethoxy-*o*-toluidine with ferric chloride, methyl being eliminated and methoxytoluquinone being formed. This is reduced to the quinol, methylated, and oxidised with permanganate.[66]

A number of papers dealing with adrenaline, the alkaloids of ergot, and compounds related to them have appeared. It is shown[67] that ergotoxine contains a carboxyl group, and that ergotinine is its lactone or lactam. A small quantity of *iso*butyrylformamide, $CHMe_2{\cdot}CO{\cdot}CO{\cdot}NH_2$, is formed in the destructive distillation of both compounds.

p-Hydroxyphenylethylamine may be synthesised in a simple manner by condensing anisaldehyde with nitromethane to β-nitro-*p*-methoxystyrene, reducing to *p*-methoxyphenylethylamine, and boiling with hydriodic acid.[68] When methyl replaces one of the hydrogen atoms of the amino-group, the physiological activity of

[64] P. Horrmann, *Ber.*, 1910, **43**, 1903; F. Angelico, *Atti R. Accad. Lincei*, 1910, [v], **19**, i, 473; *A.*, i, 577.
[65] G. Barger, *Trans.*, 1910, **97**, 466.
[66] B. D. W. Luff, W. H. Perkin, jun., and R. Robinson, *ibid.*, 1131.
[67] G. Barger and A. J. Ewins, *ibid.*, 284.
[68] K. W. Rosenmund, *Ber.*, 1909, **42**, 4778; *A.*, i, 67.

this base is very slightly reduced, but the ethyl derivative is much less active.[69] In similar manner, the compound



which differs from adrenaline only in the absence of the hydroxyl group from the side-chain, comes nearest to adrenaline in activity, but the ethyl derivative has only one-third, and the propyl derivative one-twentieth, of its activity.[70] 3 : 4-Dihydroxy-β-phenylethylamine, although so similar to adrenaline, is much less active, and 3-methyl-4-hydroxy-β-phenylethylamine is also much less active.[71]

When methylamine reacts with chloro- or bromo-hydrins of the type $C_6H_3(OMe)_2\cdot CH(OH)\cdot CH_2Cl$, compounds of both the adrenaline and *iso*adrenaline series, $C_6H_3(OMe)_2\cdot CH(OH)\cdot CH_2\cdot NHMe$ and $C_6H_3(OMe)_2\cdot CH(NHMe)\cdot CH_2\cdot OH$, are obtained.[72]

Naturally Occurring Substances.

The Acids of Bile.—The action of hydrochloric acid on ox gall yields, besides glycine and taurine, three specific acids, cholic, deoxycholic, and choleic acids, these last two being isomerides (Mylius, Langheld), and not identical, as was supposed by Latschinoff.

The three specific acids are all largely converted by nitric acid into choloidanic acid, $C_{18}H_{28}O_8$, and the mother liquors in each case contain a pentabasic acid, $C_{19}H_{28}O_{10}$ ("Letsche's acid"). Thus the three bile-acids are similarly constituted as to the grouping of nineteen carbon atoms.

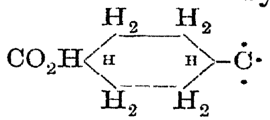
The first oxidation products of cholic acid are bilianic and *iso*bilianic acids, $C_{24}H_{34}O_8$, tribasic diketonic acids which resist somewhat energetic oxidation by potassium permanganate, and must therefore contain three totally hydrogenised carbon-ring systems.

Cilianic acid (Lassar-Cohn) is formed when bilianic acid is boiled with alkaline permanganate; according to Pregl, it has the formula $C_{20}H_{28}O_8$, and is a tricarboxylic acid, the two oxygen atoms unaccounted for being probably present in carbonyl groups, although the substance does not respond to the usual tests for ketones; from its formula and extremely stable character it may be concluded (1) that it contains two fully hydrogenised carbon-ring systems, *a* and *b*; (2) that these must be united by a straight chain of $\cdot CH_2\cdot$ groups, and (3) that the nuclei have no side groups other than

[69] G. S. Walpole, *Trans.*, 1910, **97**, 941.
[70] F. L. Pyman, *ibid.*, 264.
[71] G. Barger and A. J. Ewins, *ibid.*, 2253.
[72] C. Mannich, *Arch. Pharm.*, 1910, **248**, 127; *A.*, i, 411.

carboxyls. As cilianic acid is obtained from bilianic acid, which contains three rings, by the loss of four carbon atoms only, the presence of a six-carbon ring in this acid may be inferred, two carbon atoms being common to the rings *b* and *c*.

Cholic acid contains a double linking, for it yields an ozonide, and its ring system must be the same as that in cilianic acid, and the double linking must be present in ring (*c*). On oxidation with sulphuric acid in presence of mercury, it gives a considerable quantity of benzenepentacarboxylic acid (Schroetter), evidently arising from destruction of the naphthalene-like system (*bc*); the remaining nucleus (*a*) (termed "Panzer's ring") is almost certainly a hexahydrobenzene ring, and gives rise to the simpler benzene and hexahydrobenzene derivatives obtained from cholic acid by Panzer, whose results suggest the configuration

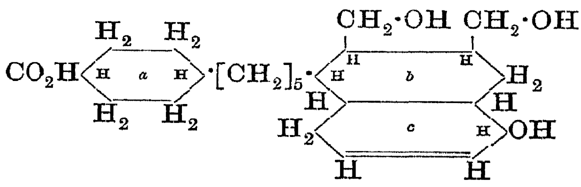


in the neighbourhood of this nucleus.

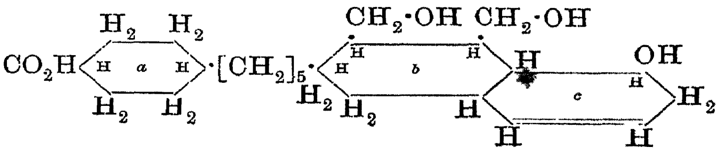
When choloidanic acid is heated, it is converted into optically active dibasic pyrocholoidanic acid, $C_{15}H_{20}O_4$, or

$$CO_2H\cdot C_6H_4\cdot C_7H_{14}\cdot CO_2H,$$

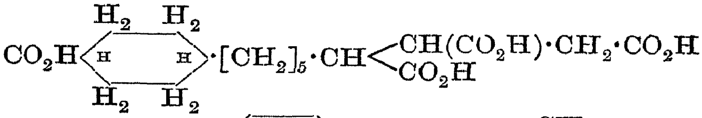
which contains a benzene nucleus, but gives a totally inactive product when heated with enough potassium permanganate to supply five atomic proportions of oxygen, a proportion corresponding with the oxidation of $\cdot CH{<}^{CH_3}_{CO_3H}$ to $\cdot CO_2H$, CO_2 and H_2O. Thus it may be inferred that the carbon atoms in this grouping formed a part of the original nucleus (*b*), for the latter is united to an unbranched chain, which consequently must be $\cdot[CH_2]_5\cdot$. This renders it necessary to represent nucleus (*b*) as a hexamethylene ring, since it presumably contains no side groups other than carboxyls. If the probable accuracy of this reasoning be admitted, then the formula of cholic acid may provisionally be represented by one or other of the two formulæ:

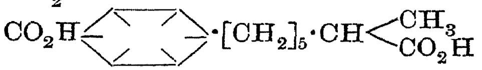


or



The position of the substituents is as yet uncertain [73]; the corresponding formulæ for choloidanic acid and pyrocholoidanic acid are respectively:

 and

 .

The latter, when heated with soda-lime, should yield *n*-heptylbenzene, and it is of interest to observe that a hydrocarbon obtained by Pregl from "cholecamphoric acid" by such treatment agrees in properties with that hydrocarbon. The isomerism of deoxycholic acid and choleic acid is also dealt with, but space does not permit further discussion of this interesting communication.

Etholides.—This curious group of natural acids present in certain coniferæ [74] are known to represent systems of condensed hydroxy-acids, into which they are resolved when submitted to hydrolysis. Among the hydrolytic products, "juniperic" and "sabinic" acids frequently occur, and these have now been identified as ω-hydroxylauric acid (I) and ω-hydroxypalmitic acid (II) respectively.

The former may be reduced to lauric acid, and oxidised to decamethylenedicarboxylic acid (II); the latter, when reduced, yields palmitic acid, and is converted by oxidising agents into tetradecamethylenedicarboxylic acid (III):

$$\text{(I.)}\quad HO\cdot CH_2\cdot[CH_2]_{10}\cdot CO_2H \longrightarrow CO_2H\cdot[CH_2]_{10}\cdot CO_2H \quad \text{(III.)}$$
$$\text{(II.)}\quad HO\cdot CH_2\cdot[CH_2]_{14}\cdot CO_2H \longrightarrow CO_2H\cdot[CH_2]_{14}\cdot CO_2H \quad \text{(IV.)}$$ [75]

Cork.—An inquiry into the nature of cork has led the investigator to the conclusion that the material is composed of an insoluble mixture of the anhydrides and polymerides of solid and liquid aliphatic acids, together with their glycerides; the young cork is probably composed of glycerides only, these being gradually hydrolysed, and the acids thus formed either undergo polymerisation or are converted into anhydrides; in support of this view, the following data are cited. A mixture of glycerides and cerin can be extracted from cork by means of indifferent solvents, such as chloroform; the insoluble residue submitted to the action of alcoholic potassium hydroxide gives 30 per cent. of acids, but the glycerides cannot be detected. The crude acids are reconverted at 140° into a brown, elastic, transparent mass, which is insoluble in indifferent solvents and impervious to gases, and if sawdust is added in the

[73] Pregl, *Zeitsch. physiol. Chem.*, 1910, **65**, 157; *A.*, i, 321.
[74] Compare *Ann. Report*, 1909, 87.
[75] J. Bougault, *Compt. rend.*, 1910, **150**, 874; *A.*, i, 297.

first instance, the product differs from cork in physical characters only in the absence of the microscopic structure peculiar to the natural substance. The main constituent to which the acid mixture owes its peculiar properties is suberic acid, which itself undergoes such a change without loss of water when heated, being apparently converted into a polymeride.[76]

Chlorophyll and Haematin.

Allusion was made in last year's report to the appearance of several important papers dealing with the constitution of chlorophyll and hæmoglobin, and further memoirs on this subject have appeared during the past year, although the progress made has been perhaps less rapid than was anticipated. The close chemical relationship which is now known to exist between these two colouring matters, so characteristic of the higher forms of vegetable and animal life respectively, has obviously great biological importance, in addition to its interest from the point of view of the structural chemist.

Hæmoglobin is actually a highly complex substance, containing a very heavy protein molecule, associated with a chromatogenic group, and it is the latter, freed from its accompanying protein, that presents itself as the analogue of chlorophyll. The presence of lecithin, long supposed to be a component of the chlorophyll molecule, has been disproved. Both colouring matters are metallic derivatives, chlorophyll containing magnesium, whilst hæmatin, from oxyhæmoglobin, is a ferric compound, the metal in each instance being held in a complex form. The relationship between the two substances was remarked as far back as 1879 by Hoppe-Seyler, who found that the spectra of phylloporphyrin and hæmatoporphyrin, coloured substances obtained as degradation products of the two pigments, and not containing a metal, resembled one another very closely. At a later date, it was shown [77] that these two compounds differ only in their oxygen-content. The further reduction of either phylloporphyrin or hæmatoporphyrin yields a volatile substance, hæmopyrrole, $C_8H_{13}N$, the constitution of which has been much disputed. It is now [78] shown to be a dimethylethylpyrrole, either

$$NH\Big<\begin{array}{l}CMe{:}CMe\\ CH{=}CEt\end{array} \quad \text{or} \quad NH\Big<\begin{array}{l}CH{=}CMe\\ CMe{:}CEt\end{array},$$

The constitution is proved by the action of nitrous acid. Whilst 2 : 4-dimethylpyrrole yields the oxime of citraconimide, the 2-methyl

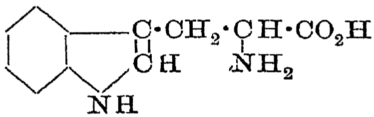
[76] M. von Schmidt, *Monatsh.*, 1910, **31**, 347 ; *A.*, i, 560.
[77] M. Nencki and J. Zaleski, *Ber.*, 1901, **34**, 997 ; *A.*, 1901, i, 434.
[78] O. Piloty and E. Quitmann, *ibid.*, 1909, **42**, 4693 ; *A.*, i, 133.

group being eliminated, hæmopyrrole, probably reacting in the same manner, yields the oxime of methylethylmaleinimide. The presence of a propyl or butyl group, once generally assumed, is thus disproved. The identity of the hæmopyrroles from chlorophyll and hæmatin, and their analogy to dimethylpyrrole, has also been shown by a comparison of the dyes which they yield with diazonium salts.[79] The principal product obtained from hæmopyrrole and benzenediazonium chloride has the formula $C_8H_{11}N(N_2Ph)_2,HCl$, but a second compound, $N_2Ph\cdot C_8H_{11}N\cdot C_8H_{11}N\cdot N_2Ph,HCl$, is formed in smaller quantity. This was at first believed to indicate the presence of a dihæmopyrrole in the original material, but it has since been found [80] that dimethylpyrrole, prepared synthetically, also yields two analogous products.

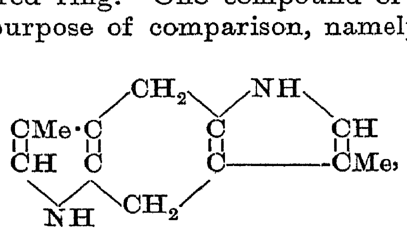
Hæmatin contains four pyrrole nuclei, of which two are probably represented by hæmopyrrole, and two by hæmopyrrolecarboxylic acid, which is either

$$NH<\begin{matrix}CMe:CMe\\ CH{=}C\cdot CH_2\cdot CH_2\cdot CO_2H\end{matrix} \quad \text{or} \quad NH<\begin{matrix}CH{=}CMe\\ CMe:C\cdot CH_2\cdot CH_2\cdot CO_2H\end{matrix}\cdot$$

As hæmatin has the formula $C_{34}H_{33}O_5N_4Fe$, it is evident that twenty atoms of hydrogen must have been eliminated in the condensation of these four groups to form the hæmatin molecule. In attempting to decide the manner in which this condensation takes place, the relationship between blood-pigment and tryptophan, which is believed, on physiological grounds, to exist, has been taken into consideration. The formula for tryptophan being



suggests that the side-chains of hæmopyrrole may be united to form a six-membered ring. One compound of this kind has been prepared for the purpose of comparison, namely, a dimethylhydropyrrindole:



by means of Knorr's synthesis from aminoacetone and ethyl succinylosuccinate. The product tends to polymerise, and yields

[79] Z. Leyko and L. Marchlewski, *Biochem. Zeitsch.*, 1909, **22**, 464; H. Malarski and L. Marchlewski, *ibid.*, 1910, **27**, 246; *A.*, i, 144, 692.

[80] L. Marchlewski and J. Robel, *Ber.*, 1910, **43**, 260; *A.*, i, 206.

dyes on oxidation, but it remains to be determined whether it bears any immediate relation to blood-pigment.[81]

The oxidation of hæmopyrrolecarboxylic acid yields hæmatic acid, which is probably the imide of Δ^{γ}-pentene-$\alpha\gamma\delta$-tricarboxylic acid [82]:

$$NH{<}\begin{matrix}CO\cdot CMe \\ CO\cdot \overset{\|}{C}\cdot CH_2\cdot CH_2\cdot CO_2H\end{matrix}$$

Each molecule of hæmatin yields two such molecules on oxidation. On the other hand, phylloporphyrin and other chlorophyll derivatives yield on oxidation one molecule of hæmatic acid and two molecules of methylethylmaleinimide, $NH{<}\begin{matrix}CO\cdot CMe \\ CO\cdot \overset{\|}{C}Et\end{matrix}$, pointing to a difference between at least two of the pyrrole nuclei in hæmatin and the corresponding groups in chlorophyll.[83]

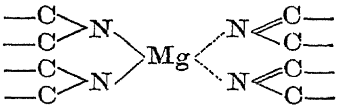
Chlorophyll is a tricarboxylic acid, and the products obtained from it by the regulated action of alkalis are di- and mono-carboxylic acids, still containing magnesium in a complex form.[84] Crystalline and amorphous chlorophyll differ only in the nature of the alcohols combined with the carboxyl groups, amorphous chlorophyll being, in part at least, an ester of the simple unsaturated alcohol phytol, $C_{20}H_{39}\cdot OH$, which is absent from the crystalline compound.[85]

The homogeneity of crystalline chlorophyll has not, however, been allowed to pass unquestioned. By the method of adsorption analysis,[86] a separation into two fractions, differing in their absorption spectra, is brought about. The two spectra are identical with those of two of the fractions formerly obtained from leaf-pigment, and now designated α- and β-metachlorophyllin respectively.[87] The degree of dependence to be placed on the method of adsorption analysis is uncertain, but a possible chemical influence of the adsorbent used would appear to be excluded by the fact that the results are not affected by the substitution of inulin for calcium carbonate.

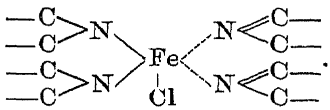
Another important question which has received much consideration is the manner in which the characteristic metal—magnesium in the case of chlorophyll, iron in that of hæmatin—is united with the remainder of the molecule. The chemical behaviour of these substances indicates that they are not salts of carboxylic

81 O. Piloty, *Ber.*, 1910, **43**, 489 ; *A.*, i, 277,
82 W. Küster, *Annalen*, 1906, **345**, 1 ; *A.*, 1906, i, 337.
83 R. Willstätter and Y. Asahina, *ibid.*, 1910, **373**, 227 ; *A.*, i, 499.
84 R. Willstätter, *Ber.*, 1909, **42**, 3985 ; *A.*, 1909, i, 979.
85 R. Willstätter and M. Benz, *Annalen*, 1907, **358**, 267 ; *A.*, 1908, i, 199.
86 M. Tsvett, *Ber. Deut. bot. Ges.*, 1906, **24**, 384 ; *A.*, 1907, ii, 144.
87 M. Tsvett, *Ber.*, 1910, **43**, 3139 ; *A.*, 1911, i. 74.

acids,[88] but that the metal is present in a complex form, linked to the iminic nitrogen of the pyrrole nuclei, the linking to carbon, assumed in the elaborate structural formulæ of Nencki and Zaleski (*loc. cit.*), being highly improbable. In view of the studies of Werner, Ley, and Tschugaeff on the complex metallic derivatives of imides, biuret, and dicyanodiamidine, a formulation involving the use of subsidiary valencies has been proposed,[89] the grouping in chlorophyll and hæmin (the hydrogen chloride compound of hæmatin) being respectively:



Chlorophyll.



Hæmin.

The iron in hæmatin, etc., is in the ferric form, the presence of ferrous iron, which has been observed in the products of fission, being due to the reducing action of the organic part of the molecule on the ferric salt formed. Hæmatin is to be regarded as containing the group $>Fe \cdot OH$, which passes into $>Fe \cdot Cl$ when this compound is converted into hæmin. The reduction of hæmatin by a variety of reagents yields hæmochromogen, the chromatogenic constituent of the hæmoglobin molecule, from which Küster concludes[90] that the reduction is confined to the iron, and that hæmoglobin is a ferrous compound. In that case oxyhæmoglobin must contain a hæmochromogen peroxide, whilst hæmatin corresponds, not with oxyhæmoglobin, but with methæmoglobin. This may be represented by the formulæ:

Hæmochromogen,	$R\vdots Fe$.
Hæmochromogen peroxide,	$R\vdots Fe<\begin{smallmatrix}O\\ \vert\\ O\end{smallmatrix}$.
Hæmatin,	$R\vdots Fe \cdot OH$.

It must be admitted, however, that the relations of hæmoglobin and oxyhæmoglobin are not yet very satisfactorily expressed by such formulæ.

Two minor points of interest arising out of recent work on hæmatin call for a brief notice.[91] The dimethyl ester of hæmin dissolves in pyridine, forming a complex in which pyridine is added at the FeCl group, recalling the behaviour of triphenylmethyl bromide in pyridine. The compound obtained by the action of

[88] This was assumed to be the case by O. Piloty and S. Merzbacher, *Ber.*, 1909, **42**, 3253, but was disproved by Willstätter, *ibid.*, 3985; *A.*, 1909, i, 857, 979.

[89] R. Willstätter and H. Fritzsche, *Annalen*, 1909. **371**, 33; *A.*, i, 126.

[90] W. Küster, *Ber.*, 1910, **43**, 370; *Zeitsch. physiol. Chem.*, 1910, **66**, 165; *A.*, i, 210, 529.

[91] W. Küster, *Ber.*, 1910, **43**, 2960, 2962; *A.*, 1911, i, 95, 69.

aniline on hæmin, and formerly described[92] as ethyl anhydrohæmaterate, proves to be merely dianilinoquinoneanil, formed by the oxidising action of the hæmin on aniline, and is not therefore in any way related to blood-pigment.

Proteins, Polypeptides, and Allied Compounds.

The development of this branch of knowledge, although of fundamental importance to biochemistry, has reached a stage when advances of general interest are comparatively rare. Every year sees substantial progress both in results and in methods of attack, but the reporter, unless an expert in the subject, can hardly form a true estimate of the relative importance of the publications which appear.

The use of β-naphthalenesulphonyl chloride has been suggested in determining the constitution of polypeptides[93]; this substance is coupled with the chloride in the usual manner, and the resulting sulphonyl derivative is hydrolysed by boiling hydrochloric acid. The β-naphthalenesulphonyl group remains in attachment to the terminal amino-acid residue, so that, on examination by Fischer's esterification method of the products from the foregoing hydrolysis, the terminal residue may be identified. A complication ensues when tyrosinyl groups are present; in this case the latter, if present as the terminal residue, appears among the hydrolytic products as di-β-naphthalenesulphonyltyrosine, otherwise the *o*-sulphonyl compound is obtained. In this way it was shown that the terminal residue in a silk peptone was alanine. Abderhalden's[94] work on the products of partial hydrolysis of proteins is proceeding; among the more recent results was the identification of dialanylglycine from silk.

Until recently it was doubtful whether the proline residue exists as such in gelatin, as α-amino-δ-hydroxyvaleric acid may be converted into proline by the action of the hydrolytic agents previously used in hydrolysing the gelatin. Barium hydroxide does not cause such a transformation, yet when used to hydrolyse gelatin an improved yield of proline is obtained, so that the latter is undoubtedly a primary product.[95]

Synthetic work in this department is making continued progress. Stachydrine (α-prolinedimethylbetaine), $CH_2<\begin{matrix}CH_2\cdot CH-CO\\ \quad\;\; | \qquad\;\; | \\ CH_2\cdot NMe_2\cdot O\end{matrix}$, a

[92] W. Küster and K. Fuchs, *Ber.*, 1907, **40**, 2021; *A.*, 1907, i, 572.

[93] E. Abderhalden and C. Funk, *Zeitsch. physiol. Chem.*, 1910, **64**, 436; *A.*, i, 320.

[94] E. Abderhalden, *ibid.*, 1909, **63**, 401; *A.*, i, 211.

[95] E. Fischer and R. Boehner, *ibid.*, 1910, **65**, 118; *A.*, i, 345.

substance present in the root-nodules of *Stachys tubifera* and in certain other plants, has been prepared synthetically by converting the ester of hygric acid (1-methylpyrrolidine-2-carboxylic acid) into its methiodide, and acting on this with silver oxide.[96]

The constitution of arginine has been definitely established as α-amino-δ-guanino-*n*-valeric acid,

$$NH:C(NH_2)\cdot NH\cdot[CH_2]_3\cdot CH(NH_2)\cdot CO_2H,$$

by a synthetic method, which consisted in condensing the α-benzoyl derivative of ornithine, $NH_2\cdot[CH_2]_3\cdot CH(NH_2)\cdot CO_2H$, with cyanamide, and hydrolysing the resulting α-benzoylamino-δ-guanino-*n*-valeric acid.[97]

The original literature should be consulted for other syntheses of important derivatives of pyrrolidine[98] and its carboxylic acid.[99]

Condensation products of amino-acids with glycerol have been prepared in order to examine their behaviour, especially towards hydrolytic agents.[1] The results may assume significance in later developments of protein chemistry, and the same remark applies to those obtained in an examination of certain polypeptides which are produced by condensing amino-acids with amino-aldehydes,[2] and possibly future reporters may have occasion to enlarge upon these points.

Certain acylated amino-acids are readily converted into compounds which are now regarded as lactones derived from a group $\cdot CO\cdot NH\cdot$, functionating in the enamic[3] form $\cdot C(OH):N\cdot$. Thus anthranoylanthranilic acid, with excess of acetic anhydride, does not yield a simple acetyl derivative, as previous workers had supposed, but the lactone, $NHAc\cdot C_6H_4\cdot C{<}{\begin{smallmatrix}N\cdot C_6H_4\\ \vert \\ O-CO\end{smallmatrix}}$. "Acetylanthranil" has the structure ${\begin{smallmatrix}CMe:N\\ \vert \\ O-CO\end{smallmatrix}}{>}C_6H_4$ and benzoylanthranilic acid is similarly constituted.

A number of other acylated amino-acids, for instance, benzoylalanine, yield compounds of this type, which are intermediate in properties between lactones and acid anhydrides. They combine readily with ammonia, with scission of the lactone ring, and the products, when heated with alkalis, are converted into lactimes or

96 E. Schulze and G. Trier, *Ber.*, 1909, **42**, 4654 ; *A.*, i, 62.

97 S. P. L. Sörensen, *ibid.*, 1910, **43**, 643, *A.*, i, 227.

98 E. Fischer and A. Luniak, *ibid.*, 1909, **42**, 4752 ; *A.*, i, 136.

99 E. Fischer and G. Zemplén, *ibid.*, 4878 ; *A.*, i, 100, etc.

1 E. Abderhalden and M. Guggenheim, *Zeitsch. physiol. Chem.*, 1910, **65**, 53 ; *A.*, i, 226

2 C. D. Harries and I. Petersen, *Ber.*, 1910. **43**, 634 ; *A.*, i, 228.

3 Compare *Ann. Report*, 1909, 100.

cyclic imides, corresponding with the original lactones; for example:

$$NHAc\cdot C_6H_4\cdot C{<}{\begin{matrix}N{-}{-}C_6H_4\\ NH\cdot CO\end{matrix}}.^{4}$$

Dipeptides containing the residues of some of the higher fatty acids have recently been synthesised in view of their possible physiological importance. Thus, for example, α-amino-*n*-nonylglycine, $NH_2\cdot C_8H_{16}\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$, was formed by converting α-bromononyl chloride into α-bromo-*n*-nonoylglycine, and acting on the latter with ammonia.

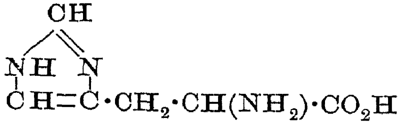
Similar compounds, containing the residues of alanine and leucine, as well as the corresponding lauryl compounds, were isolated.[5]

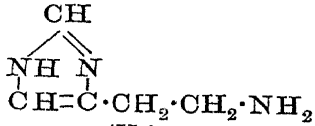
A tetrapeptide, glycylaspartyldiglycine,

$$NH_2\cdot CH_2\cdot CO\cdot NH\cdot CH{<}{\begin{matrix}CO\cdot NH\cdot CH_2\cdot CO_2H\\ CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2H\end{matrix}},$$

has been prepared synthetically,[6] and a number of dipeptides of serin,[7] which have an interest in connexion with certain natural proteins.

The bacterial cleavage of histidine (I) under anærobic conditions leads in certain circumstances to the formation of carbon dioxide and β-amino-4-ethylglyoxaline (II), thus proving that the amino-group is present in the α-position with respect to the carboxyl group, a matter which heretofore[8] has been somewhat uncertain:


(I.)


(II.)

Enzymes.

The authors of this report have carefully considered the desirability of inserting chapters discussing the more important results obtained during the last few years in the study of enzyme action, including fermentation. The subject, although of the utmost importance and intimately associated with organic chemistry, demands for its proper exposition a special and intimate knowledge to which the present writers cannot lay any claim; for this reason, also, their estimate of the relative importance of the

[4] E. Mohr and F. Köhler, *J. pr. Chem.*, 1909, [ii], **80**, 521; E. Mohr and T. Geis, *ibid.*, **81**, 49; E. Mohr and F. Stroschein, *ibid.*, 473; *A.*, i, 116, 117, 483.
[5] A. Hopwood and C. Weizmann, *Proc.*, 1910, **26**, 69.
[6] E. Fischer and A. Fiedler, *Annalen*, 1910, **375**, 181; *A.*, i, 656.
[7] E. Fischer and H. Roesner, *ibid.*, 199; *A.*, i, 657.
[8] D. Ackermann, *Zeitsch. physiol. Chem.*, 1910, **65**, 504; *A.*, i, 419.

published contributions in this field is not likely to be an accurate one, and they therefore prefer to make no selection from the mass of experimental data on record. In connexion with fermentation, however, attention may be drawn to a useful summary of recent views on the mechanism of the process,[9] as well as to an important mathematical paper on the "Rôle of Diffusion in Fermentation by Yeast Cells."[10]

A short reference may be made to some controversial work on the oxydases and peroxydases. The view was originally propounded by Bertrand that these substances are complex organic compounds of manganese, and it is stated[11] that even after purification has been carried so far that all coagulable proteins have been removed, minute quantities of manganese always remain. No relation, however, could be traced between the proportion of manganese and the activity of the oxydase, and other workers claim that active preparations may be obtained free from either manganese or iron.[12] Metallic salts accelerate the action, manganese salts being particularly active in certain cases, and the function of the metal appears to be, like that of a peroxydase, the transference of oxygen from the peroxide initially formed to the oxidisable substance. On this view, the action of oxydases is a chemical process, exactly comparable with the oxidation of indigotin by air in the presence of benzaldehyde.[13] The autoxidation of organic compounds containing amino- and hydroxy-groups in presence of copper has been studied in some detail,[14] and it is found that metallic copper is not only dissolved by ammonia in contact with air, but also by solutions of amines, and of glycols, glycerol, or mannitol. The copper in such cases evidently forms complex compounds, which act as carriers of oxygen. In view of the fact that oxyhæmoglobin, which contains iron in a complex form, behaves like an organic peroxydase,[15] the nature of the part played by complexes containing metals in reactions of this kind calls for a more thorough investigation.

As bearing on this point, attention may be called to experiments on the direct chemical action of organic peroxides on unsaturated compounds. Thus, benzoyl hydroperoxide, $C_6H_5{\cdot}CO{\cdot}O{\cdot}OH$, oxidises

[9] Miss O. E. Ashdown and J. T. Hewitt, *Trans.*, 1910, **97**, 1636.
[10] A. Slator and H. J. S. Sand, *ibid.*, 922.
[11] A. W. van der Haar, *Ber.*, 1910, **43**, 1321, 1327 ; *A.*, i, 604.
[12] A. Bach, *ibid.*, 364, 366, *Arch. Sci. phys. nat.*, 1910, [iv], **30**, 152 ; *A.*, i, 291, 801.
[13] See also R. A. Gortner, *Trans.*, 1910, **97**, 110 ; H. Euler and I. Bolin, *Zeitsch. physikal. Chem.*, 1909, **69**, 187 ; *A.*, i, 84.
[14] W. Traube, *Ber.*, 1910, **43**, 763 ; *A.*, i, 294.
[15] J. Wolff and E. de Stoeklin, *Compt. rend.*, 1910, **151**, 483 ; *A.*, i, 802.

olefines, geraniol, limonene, and a number of other substances to oxides,[16] and converts aniline into either azobenzene or nitrosobenzene, according to the proportions used, whilst acetyl or benzoyl peroxide may be used for the oxidation of diphenylamine, acyldiphenylhydroxylamine being formed at first, and then undergoing molecular rearrangement, with the formation of several more complex derivatives.[17]

Organic Compounds of Sulphur.

Certain phases in the study of these compounds are of general interest, and investigations include studies of compounds having a biochemical importance, while others throw light on problems of isomeric change and, more generally, the influence of residual affinities on physical and chemical properties. The latter aspect of the chemistry of sulphur is especially interesting when reviewed in connexion with the influence of oxygen in modifying physical and chemical properties, and rapid developments may be anticipated from a comparative study of the effects produced by these two related elements.

A few instances of the influence of sulphur in modifying the properties of compounds may be mentioned. The absorption of light by sulphur compounds is much greater than that of the corresponding oxygen compounds, and the following atomic groups give rise to definite absorption bands which are not given by their oxygen analogues:

$$\mathrm{S{:}C}{<}\begin{matrix}\mathrm{O-}\\\mathrm{O-}\end{matrix},\quad \mathrm{S{:}C}{<}\begin{matrix}\mathrm{S-}\\\mathrm{O-}\end{matrix},\quad \mathrm{S{:}C}{<}\begin{matrix}\mathrm{S-}\\\mathrm{S-}\end{matrix},\quad \mathrm{O{:}C}{<}\begin{matrix}\mathrm{S-}\\\mathrm{S-}\end{matrix},\quad \begin{matrix}\mathrm{\cdot S\cdot C{:}O}\\ \quad\; | \\\mathrm{\cdot S\cdot C{:}O}\end{matrix},\quad \begin{matrix}\mathrm{\cdot S\cdot C{:}O}\\ \quad\; | \\\mathrm{\cdot O\cdot C{:}O}\end{matrix}\cdot$$

whilst the characteristic bands of phenol and benzyl alcohol are obliterated when the oxygen is replaced by sulphur, owing to the influence of the latter element on the distribution of residual affinity in the ring.[18]

The influence of sulphur in rendering active an adjacent methylene group is also very remarkable, the two methylene groups in ethyl thiodiglycollate, $\mathrm{S}{<}\begin{matrix}\mathrm{CH_2\cdot CO_2Et}\\\mathrm{CH_2\cdot CO_2Et}\end{matrix}$, being highly reactive, condensing readily with *a*-diketones, *o*-quinones, and similar compounds. The influence of the carbethoxy-group in producing

[16] N. Prileschaéeff, *Ber.*, 1909, **42**, 4811; 1910, **43**, 959; E. Lippmann, *ibid.*, 464; *A.*, i, 86, 149, 295.

[17] S. Gambarjan, *ibid.*, 4003; *A.*, 1909, i, 910.

[18] J. E. Purvis, H. O. Jones, and H. S. Tasker, *Trans.*, 1910, **97**, 2287.

activity is small, so that the effect must be attributed chiefly to the sulphur.[19]

The sulphone group, SO_2, influences an adjacent methylene group in the same manner, so that the compounds $R{\cdot}SO_2{\cdot}CH_2{\cdot}CN$, $R{\cdot}SO_2{\cdot}CH_2{\cdot}CO{\cdot}NH_2$, and $R{\cdot}SO_2{\cdot}CH_2{\cdot}CO_2Et$ show reactivity of a kind similar to that exhibited by compounds in which CO takes the place of SO_2, although the properties naturally vary greatly with the nature of the group adjacent to the methylene group.

Cheirolin.—Remarkable results have been obtained during the examination of the alkaloid-like compound present in wallflower seeds,[20] which was identified as a methylsulphone of propylthiocarbimide, such a structure being probably unique among naturally occurring substances; its synthesis has been accomplished in the following manner.

Methyl γ-phthaliminopropyl sulphide (I), obtained from sodium methylmercaptide and γ-bromopropylphthalimide, was converted by hydrolysis into phthalic acid and methyl γ-aminopropyl sulphide (II). The latter, in the form of its hydrochloride, was oxidised to the corresponding sulphone (III), which was converted by carbon disulphide, in accordance with Hofmann's method, into cheirolin (IV)[21]:

$$C_6H_5{<}{\genfrac{}{}{0pt}{}{CO}{CO}}{>}N{\cdot}C_3H_6{\cdot}S{\cdot}CH_3 \quad \text{(I.)} \qquad NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}CH_3 \quad \text{(II.)}$$

$$NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}SO_2{\cdot}CH_3 \quad \text{(III.)} \qquad S{:}C{:}N{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}SO_2{\cdot}CH_3 \quad \text{(IV.)}$$

During the last decade, Autenrieth and his collaborators have shown that certain dihydric mercaptans readily condense with aldehydes and ketones, forming compounds which contain six-, seven-, or sixteen-membered rings containing sulphur. The work has recently been extended to the formation of rings from the para- and meta-xylylene dihydrosulphides. *p*-Xylylene hydrosulphide condenses with aromatic aldehydes to form compounds containing eighteen-membered heterocyclic rings; with benzaldehyde and hydrochloric acid it yields duplo-*p*-xylylenebenzylidenemercaptal:

$$C_6H_4{<}{\genfrac{}{}{0pt}{}{CH_2{\cdot}S{\cdot}CHPh{\cdot}S{\cdot}CH_2}{CH_2{\cdot}S{\cdot}CHPh{\cdot}S{\cdot}CH_2}}{>}C_6H_4.$$

Similarly constituted substances, but with smaller rings, are formed when *m*-xylylene hydrosulphide is used.[22]

Work has also been undertaken bearing on the relative stability

[19] O. Hinsberg, *Ber.*, 1910, **43**, 901; *A.*, i, 334.

[20] Compare Wagner, *Chem. Zeit.*, 1908, **32**, 76; *A.*, 1908, i, 202.

[21] W. Schneider, *Annalen*, 1910, **375**, 207; *A.*, i, 658.

[22] W. Autenrieth and F. Beuttel, *Ber.*, 1909, **42**, 4346, 4357, *A.*, i, 60, 61.

of rings containing different numbers of carbon atoms united with the sulphur atom, and the ring (I) is then found to be formed readily, whilst (II) is only obtained with difficulty[23]:

$$\begin{matrix} CH_2\cdot CH_2 \\ | \\ CH_2\cdot CH_2 \end{matrix}\!>\!S \qquad\qquad CH_2\!<\!\begin{matrix} CH_2\cdot CH_2 \\ CH_2\cdot CH_2 \end{matrix}\!>\!S$$

(I.) (II.)

Aromatic disulphides are decomposed at 240—280° into mixtures of monosulphides and trisulphides, and in certain cases nearly in the proportions required by the equation:

$$2S_2Ph_2 = SPh_2 + S_3Ph_2.$$[24]

The presence of substituting groups, such as carboxyl, in the aromatic nucleus does not materially alter the course of the reaction, although secondary products, such as thioanhydrides, may be formed.

Organic sulphides in which the sulphur is directly attached to a methyl or methylene group combine with a molecular proportion of halogen; if the two groups attached to sulphur are both aromatic in type, this reaction does not take place. Similarly, the derived sulphoxides yield dibromides on treatment with hydrogen bromide only if the sulphoxy-group is not in attachment to two aromatic nuclei.[25]

The reactivity of mercaptan and also the oxidising power of sulphur dioxide is shown in a striking manner when they act on one another in glacial acetic acid; in presence of hydrogen chloride, a mixture of benzyl disulphide and benzyl trisulphide is formed in quantitative amount, as represented by the equation:

$$4C_6H_5\cdot CH_2\cdot SH + SO_2 = (C_6H_5\cdot CH_2)_2S_2 + (C_6H_5\cdot CH_2)_2S_3 + 2H_2O.$$[26]

Phosphorescent Sulphur Compounds.—Certain derivatives of thiocarboxylic acids are oxidised by air at the ordinary temperature, emitting fumes which are luminous in the dark. The effect appears to be associated with the presence of the group $S\colon\dot{C}\cdot O\cdot$ in the molecule, and, in the series which exhibit it, is more pronounced with the volatile members. Dithiocarbonic esters, $OR\cdot CS\cdot SR'$, thiocarbamic esters, $NR_2\cdot CS\cdot OR$, as well as the esters $CS(OMe)_2$ and $Me\cdot CS\cdot OMe$, and chlorides of the type $Cl\cdot CS\cdot OMe$, all behave in this manner, but the isomeric compounds containing the group $\cdot S\cdot\ddot{C}\cdot O\cdot$ are inert. It would thus appear that the grouping $S\colon\dot{C}\cdot$ has an exceptionally high residual affinity.[27]

[23] J. von Braun and A. Trümpler, *Ber.*, 1910, **43**, 545 ; *A.*, i, 274.

[24] O. Hinsberg, *ibid.*, 1874 ; *A.*, i, 553.

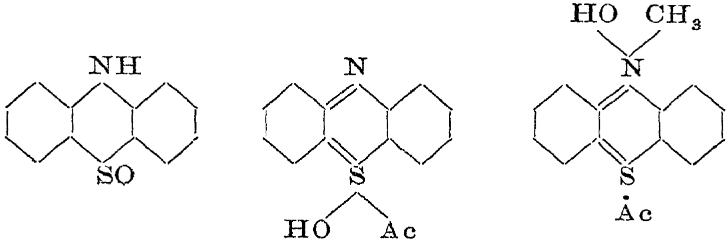
[25] E. Fromm and G. Raiziss, *Annalen*, 1910, **374**, 90 ; *A.*, i, 554.

[26] J. A. Smythe and A. Forster, *Trans.*, 1910, **97**, 1195.

[27] M. Delepine, *Compt. rend*, 1910, **150** 876 ; *Bull. Soc. chim.*, 1910, [iv], **7**, 722, 724 ; *A.*, i, 295, 612, 613.

The luminescence of thiocarbamic esters is found to be stimulated by alkalis, and in open vessels proceeds to completion, neither ozone nor hydrogen peroxide being produced. It has been suggested that an unstable peroxide is first formed, which decomposes into carbamate and sulphur monoxide, which reacts with the alkali, yielding thiosulphate; salts of another acid, $H_2S_3O_5$, intermediate between sulphurous and thiosulphuric acid, are also said to be formed.[28]

Isomeric Change in Sulphur Derivatives.—It has been found that the ortho-sulphoxides of diphenylamine (type I) are transformed by the action of acid reagents into the corresponding azothionium derivatives (type II):



(I.) (II.) (III.)

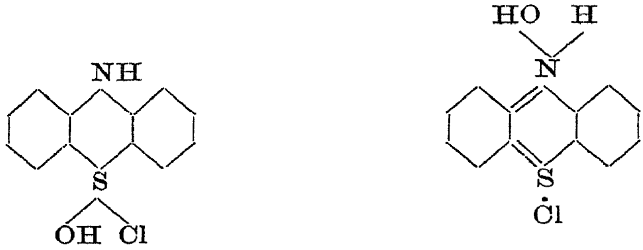
The product which is obtained by the action of acids on *N*-methyldiphenylamine *o*-sulphoxide is of similar character to that obtained from the parent compound, and, since it yields *N*-methylthiodiphenylamine on reduction, and *N*-methylchlorothiodiphenylamine by the further action of halogen acid, it is clear that the *N*-alkyl group of the sulphoxide has not suffered transposition during the change. The substance is accordingly represented by the formula III. Assuming that the reaction pursues the same course with the imino-compounds as with the *N*-alkyl derivatives, it is evident that with the former the change does not proceed by direct migration of iminic hydrogen.[29]

The mechanism of the reaction has been further discussed with data obtained from the study of the relative speeds of change in different sulphoxides with acids of varying strength, and it is concluded that the reaction in question depends on the preliminary formation of a salt of the sulphoxide, which by some further process is transformed into the sulphonium derivative. This conclusion has been confirmed by the isolation of the hydrochloride of trichlorodiphenylamine *o*-sulphoxide, which is very readily transformed into the azothionium derivative when gently warmed in

[28] O. Billeter, *Ber.*, 1910, **43**, 1833; *A.*, i, 564.

[29] Barnett and Smiles, *Trans.*, 1909, **95**, 1253; 1910, **97**, 186; Brady and Smiles, *ibid.*, 1910, **97**, 1559.

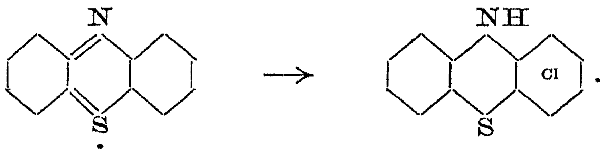
certain media. It is clear that the conversion of the sulphoxide salt (IV) into the azothionium derivative proceeds either by separation of the elements of water or by migration of hydroxyl



(IV). (V.)

from quadrivalent sulphur to tervalent nitrogen. The latter alternative appears to be correct, as in all the cases studied the azothionium compounds contain an additional molecule of water, which seems to be present in an ammonium hydroxide complex (V), as is also the case with the *N*-methyl derivative (III).

In presence of excess[30] of hot halogen acids, these phenazothionium salts are capable of further intramolecular change, being converted into halogen derivatives of thiodiphenylamine. Thus, with excess of hydrochloric acid, phenazothionium chloride yields chlorothiodiphenylamine (VI), and a similar change takes place with the *N*-methyl derivative:



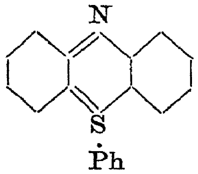
(VI.)

Since diphenylamine *o*-sulphoxide (I) is obtained by the action of hydrogen peroxide on thiodiphenylamine, it would seem that the process of chlorination of the latter substance takes place in three stages, namely, production of (1) sulphoxide, (2) sulphonium chloride, and (3) the chloro-substitution derivative, each of which may be isolated.

The additional knowledge of phenazothionium derivatives obtained in examining these intramolecular changes has been applied to the further study[31] of the *S*-phenylphenazothionium

[30] Page and Smiles, *Trans.*, 1910, **97**, 1112.
[31] Barnett and Smiles, *ibid.*, 362.

group. The structure



(VII.)

which was previously assigned [32] to the products obtained from the condensation of aromatic substances with certain sulphoxides of diphenylamine, is now certain, and the analogy between these substances and the parent phenazothionium group is demonstrated. This study of the phenazothionium group is brought to a conclusion in a paper [33] dealing with the *S*-alkyl derivatives which are obtained from thiodiphenylamine by the addition of alkyl iodide in presence of mercuric iodide. Under these conditions the alkyl iodide unites with the bivalent sulphur group, and mercuri-iodides of the alkylated bases are obtained. These alkylated bases seem to be stable only in the form of the double salt, for on removing the metal by the usual means, the alkyl group is eliminated. However, silver hydroxide attacks the methyl derivative (VIII), yielding very small quantities of the quinonoid *S*-methylphenazothionium base.

Selenophen, $\begin{matrix} CH{:}CH \\ | \\ CH{:}CH \end{matrix}\!\!>Se$, may appropriately be mentioned in this section. It has been obtained by heating sodium succinate with phosphorus triselenide, and forms a yellow, mobile, irritant liquid.[34]

It is not pretended that the foregoing selection of subjects includes all the most important advances of the year 1910, or that the investigations selected are of superior value to those omitted. The necessity of choosing a few topics from the mass of published work of the year involves the omission of much that is interesting and important, whilst a certain degree of arbitrariness unavoidably attaches to the selection of topics for discussion. It is hoped, however, that the brief summaries of progress in certain departments of organic chemistry may be of assistance in guiding the student, who can trace the more detailed development of any branch by means of the annual index. The theories of organic chemistry are in a state of transition, and it may well be that the reporters of a few years hence may find the systematisation of their material an easier task than at present, owing to the

[32] *Ann. Report*, 1908, 166.
[33] Barnett and Smiles, *Trans.*, 1910, **97**, 980.
[34] Foa, *Gazzetta*, 1909, **39**, ii, 527 ; *A.*, i, 187.

advance in knowledge of the relations between the structure and properties of organic compounds. It is impossible to resist the conclusion that many of the partial explanations adopted at the present time are tentative, and are destined to be embraced in wider generalisations, which will have the effect of giving to this branch of chemistry a far greater degree of homogeneity and symmetry than it now possesses.

CECIL H. DESCH.
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ANALYTICAL CHEMISTRY.

ALTHOUGH, as the writer has previously observed, it is extremely difficult to give a connected critical review of the progress that has been achieved in this branch of chemistry during the year, he ventures to think that, in the present report, it has been possible to piece together several interesting observations into what may be termed historical paragraphs. The quality of the papers published in 1910 appears to have improved. Not only have an exceptional number of new suggestions been made, but additional activity is being shown in the no less important direction of revising existing methods with the view of increasing their accuracy or of placing them on a sounder scientific basis. Despite this, a reviewer cannot fail to discern that a leaning towards novelty, often at the expense of utility, is still in evidence. This is perhaps particularly noticeable in researches emanating from physiological laboratories. When a method is required for a certain purpose for which there may exist one, if not more, of known accuracy, the physiologist, instead of making himself acquainted with these, devises a fresh one, which, as often as not, is unsound and untrustworthy. It is a healthy sign, however, that limit of accuracy is receiving increasing attention from most investigators, although there are still numerous instances in which necessary precautions are neglected, whilst in others ridiculous and unnecessary refinements are adopted. Further, it is still true that some of the problems that have been worked out can at best be described as mere students' exercises leading to no useful results. The Society of Public Analysts and other Analytical Chemists has undoubtedly done much by its investigation scheme in indicating problems that await solution, and the number of researches carried out under the terms of the scheme, although as yet small, quite justifies its existence. Increasing utility may be anticipated to accrue from it in the future.

General.

A decomposition flask for use in conjunction with the nitrometer has been devised by E. Berl and A. W. Jurrisen.[1] It is adapted for the estimation of nitrogen in smokeless powders, and may also

[1] *Zeitsch. angew. Chem.*, 1910, **23**, 241; *A.*, ii, 240.

be used [2] for the assay of calcium carbide, sodium amalgam, and zinc dust. E. Berl [3] describes some ingenious absorption and extraction apparatus, and also two forms of weighing pipette—one a modification of that devised by Lunge and Rey for weighing liquids such as "oleum," and another for weighing liquids of high vapour tension. Apparatus for the estimation of sulphur trioxide in "oleum" has been devised by G. Finch [4] and by R. H. Vernon.[5]

F. Emich and J. Donau [6] describe an apparatus by means of which small quantities of precipitates—a few milligrams—may be collected. The method may be applied quantitatively in conjunction with a Nernst micro-balance.

A simple and efficient fractionating column has been devised by A. Hahn.[7] Its action depends on the presence of a cooling liquid, maintained at its boiling point by the vapours of the liquid being fractionated, which thus acts as a dephlegmator. Whilst it requires no attention, it is shown that mixtures of ether and alcohol, methyl and ethyl alcohol, and methyl ethyl ketone and diacetyl have been successfully fractionated. In attempting to fractionate a liquid under diminished pressure with the ordinary form of dephlegmator, a considerable amount of liquid is often condensed in the column. To obviate this, L. Bouveault [8] has devised a still-head which is too wide for the formation of a long layer of condensed liquid.

A desiccator, which can be exhausted and also heated, is described by J. Hladík.[9]

A. Kleine [10] has devised an apparatus for the estimation of sulphur and arsenic in iron and steel, whilst another apparatus for the estimation of carbon sulphur and arsenic in iron and steel is described by G. Preuss,[11] and also an apparatus for the estimation of sulphur.[12] For the estimation of arsenic by the Gutzeit method, an apparatus has been devised by H. Kasarnowski.[13]

P. A. Kober [14] upholds the accuracy of the aeration method of distilling off ammonia from a solution.

[2] *Zeitsch. angew. Chem.*, 1910, **23**, 248; *A.*, ii, 242.
[3] *Chem. Zeit.*, 1910, **34**, 428; *A.*, ii, 538.
[4] *Zeitsch. ges. Schiess. und Sprengstoffwesen*, 1910, **5**, 167.
[5] *Chem. Zeit.*, 1910, **34**, 792; *A.*, ii, 803.
[6] *Monatsh.*, 1909, **30**, 745; *A.*, ii, 152.
[7] *Ber.*, 1910, **43**, 419; *A.*, ii, 183.
[8] *Bull. Soc. chim.*, 1910, [iv], **7**, 273; *A.*, ii, 485.
[9] *Biochem. Zeitsch.*, 1910, **28**, 29; *A.*, ii, 930.
[10] *Chem. Zeit.*, 1910, **34**, 636; *A.*, ii, 749.
[11] *Zeitsch. angew. Chem.*, 1910, **23**, 1980; *A.*, ii, 1109.
[12] *Chem. Zeit.*, 1910, **34**, 840; *A.*, ii, 893.
[13] *Ibid.*, 299; *A.*, ii, 451.
[14] *J. Amer. Chem. Soc.*, 1910, **32**, 689; *A.*, ii, 661.

The solvent properties of trichloroethylene ("Westrosol") have been investigated by L. Gowing-Scopes.[15] A non-inflammable liquid, boiling at 88°, it dissolves mercuric halides, nitrous acid, ammonia, hydrogen sulphide, chlorine, bromine, iodine, and sulphur, besides most organic compounds that do not contain two or more carboxyl or hydroxyl groups. Although withstanding the action of alkalis, it cannot, as an unsaturated compound, be used in presence of oxidising agents.

L. Gutmann[16] describes an improved form of Kipp's apparatus, which, without taking it to pieces, enables the spent liquid to be drawn off. An apparatus which gives a constant supply of either hydrogen sulphide or its saturated solution has been devised by S. Urbasch.[17]

A modified Soxhlet extraction apparatus is described by J. M. Sanders[18]; it enables the solvent to be distilled off after the extraction is complete without disconnecting the apparatus. It appears, however, to occupy much more room laterally than the ordinary Soxhlet extractor.

Physical Analysis.

Among physical methods that have been called into use in analytical chemistry must be mentioned the proposal of W. Hempel and R. von Klemperer[19] to estimate potassium in presence of sodium (1 : 8), and calcium in presence of sodium (1 : 100) spectrometrically. The method can also be applied to the estimation of lithium and of thallium. It is specially recommended for soil analysis.

P. Dutoit[20] shows that the point of complete precipitation may be determined by electrical conductivity measurements. If, for instance, successive quantities of a concentrated solution of an iodide are added to a dilute solution of a silver salt by means of a capillary burette capable of being read to 0·001 c.c., and the conductivity after each addition is plotted as a function of the volume of precipitant added, two approximately straight lines are obtained which intersect at a point corresponding with complete precipitation. The temperature must not vary within $\pm 0{\cdot}1°$. In conjunction with P. Mojoïu,[21] he has applied this method to the volumetric estimation and separation of the alkaline earth metals.

[15] *Analyst*, 1910, **35**, 238; *A.*, ii, 647.
[16] *Zeitsch. angew. Chem.*, 1910, **23**, 728; *A.*, ii, 493.
[17] *Chem. Zeit.*, 1910, **34**, 1040; *A.*, ii, 949.
[18] *Proc.*, 1910, **26**, 227.
[19] *Zeitsch. angew. Chem.*, 1910, **23**, 1756; *A.*, ii, 995.
[20] *J. Chim. phys.*, 1910, **8**, 12; *A.*, ii, 342.
[21] *Ibid.*, 27; *A.*, ii, 343.

For polarimetric purposes, the oxygenated salts of sodium are recommended as giving very intense flames, for example, nitrates, nitrites, chlorates, etc. The flames are said to be sufficiently strong to enable the rotatory power of osazones to be determined.[22]

Gas Analysis.

A new principle has been suggested for the separation of gases by E. Erdmann and H. Stoltzenberg,[23] namely, that of fractional condensation by liquid air, liquid oxygen, solid ether, alcohol, and carbon dioxide. It has been applied with results of the highest accuracy to the analysis of the following gaseous mixtures: ethylene and hydrogen, ethylene and oxygen, carbon dioxide and oxygen, nitrous oxide and oxygen. Probably it will be of service chiefly in supplementing the ordinary methods. Apparatus for this new method is described by H. Stoltzenberg.[24] Equally novel is the proposal of C. Paal and W. Hartmann[25] to absorb hydrogen in gaseous mixtures by a solution of colloidal palladium and picric acid. In these circumstances, the picric acid is reduced by the hydrogen, the palladium acting as a catalyst. If any of the constituents present in a mixture besides hydrogen are absorbable, they must be removed previously by ordinary reagents. The use of a *solution* of phosphorus in castor oil, instead of the solid substance, for absorbing oxygen from gaseous mixtures has been suggested by M. Centnerszwer.[26] A refractometric method for the analysis of gaseous mixtures has been devised by L. Stuckert.[27] By its means, 0·01 per cent. of methane can be detected in air, but here it must be observed that, as in all physical methods, the method can only be used with certainty when the constituents of a mixture are known. The refractive indices of a number of gases are given, the determinations having been made by a Jamin interferometer.

E. Hintz and L. Grünhut[28] deal with the estimation of methane in gases from natural springs, whilst F. Henrich[29] has improved Fresenius's method of estimating hydrocarbons in natural gases, and describes a new apparatus for the purpose.

For technical gas analysis, A. H. Elliott has devised an apparatus for the analysis of illuminating gas,[30] which, according to E. C.

22 C. Neuberg, *Biochem. Zeitsch.*, 1910, **24**, 423; *A.*, ii, 446.
23 *Ber.*, 1910, **43**, 1702; *A.*, ii, 649.
24 *Ibid.*, 1708; *A.*, ii, 649.
25 *Ibid.*, 243; *A.*, ii, 237.
26 *Chem. Zeit.*, 1910, **34**, 494; *A.*, ii, 541.
27 *Zeitsch. Elektrochem.*, 1910, **16**, 37; *A.*, ii, 245.
28 *Zeitsch. anal. Chem.*, 1910, **49**, 25; *A.*, ii, 356.
29 *Zeitsch angew. Chem.*, 1910, **23**, 441; *A.*, ii, 355.
30 *J. Soc. Chem. Ind.*, 1910, **29**, 192; *A.*, ii, 353.

Uhlig,[31] gives results agreeing well with those obtained when Hempel's apparatus is used. Uhlig[32] describes an apparatus for the analysis of oil gas. He has tested Elliott's photometric lamp, and finds it very constant.[33] G. N. Huntley[34] describes a useful gas sampling tube, suitable for taking samples of flue gases. A. Gwiggner[35] describes a modified Hempel burette,[36] and L. L. de Koninck[37] a modification of Nowicki's gas-absorption pipette.

A form of the Toepler pump has been devised by B. D. Steele,[38] by means of which the gas from the apparatus being exhausted may be collected. A simplified form of the Toepler pump is also described by A. von Antropoff.[39]

G. Calvi[40] gives a description of a new apparatus for the estimation of carbon dioxide in air by Lunge and Zeckendorf's method.

Indicators.

Some important communications have been made during the year on the ionic theory of indicators and on the measurement of the concentration of hydrogen and hydroxyl ions in a solution colorimetrically.[41] E. Vassallo[42] ascribes the disappearance of colour on adding concentrated alkali to phenolphthalein to the re-formation of the lactone form. It has been shown that 2 : 5-dinitroquinol is a compound giving a very wide range of colours with different acids and bases, and it has been recommended for the estimation of the concentration of hydrogen and hydroxyl ions in unknown solutions.[43] None of these papers permits of useful condensation. A new indicator, said to be equal in sensitiveness to phenolphthalein, is 6-sulpho-β-naphthol-1-azo-*m*-hydroxybenzoic acid.[44] α-Naphtholphthalein is said to be an indicator the sensitive point of which is very close to neutrality, the concentration of hydrogen ions at this point being between $10^{-7 \cdot 26}N$ and $10^{-8 \cdot 68}N$.[45]

[31] *J. Soc. Chem. Ind.*, 1910, **29**, 194 ; *A.*, ii, 354.
[32] *Ibid.*, 196 ; *A.*, ii, 354.
[33] *Ibid.*, 197.
[34] *Ibid.*, 196 ; *A.*, ii, 354.
[35] *Zeitsch. angew. Chem.*, 1910, **23**, 642 ; *A.*, ii, 445.
[36] Compare also L. L. de Koninck, *Bull. Soc. chim. Belg.*, 1910, **24**, 231 ; *A.*, ii, 648.
[37] *Ibid.*, 233 ; *A.*, ii, 648.
[38] *Phil. Mag.*, 1910, [vi], **19**, 863 ; *A.*, ii, 602.
[39] *Chem. Zeit.*, 1910, **34**, 979 ; *A.*, ii, 947.
[40] *Giorn. Farm. Chim.*, 1910, **59**, 289.
[41] See A. A. Noyes, *J. Amer. Chem. Soc.*, 1910, **32**, 815 ; *A.*, ii, 746 ; H. T. Tizard, *Trans.*, 1910, **97**, 2477.
[42] *Boll. Chim. Farm.*, 1910, **49**, 345.
[43] L. J. Henderson and A. Forbes, *J. Amer. Chem. Soc.*, 1910, **32**, 687 ; *A.*, ii, 541.
[44] R. Mellet, *Chem. Zeit.*, 1910, **34**, 1073 ; *A.*, ii, 995.
[45] S. P. L. Sörensen and S. Palitzsch, *Biochem. Zeitsch.*, 1910, **24**, 381 ; *A.*, ii, 446.

Inorganic Chemistry.

Qualitative.—The scheme of Abegg and Herz[46] for the detection and separation of the more important negative ions has been revised and modified by T. Milobendski.[47] He claims to have rendered it much more precise.

A delicate reagent for the detection of nitric acid is said to be a solution of di-9(10)-hydroxyphenanthrylamine in concentrated sulphuric acid, which changes by oxidation from blue to wine red. Nitrous acid also gives the reaction, but much larger quantities are required, and when it occurs it is owing to the formation of nitric acid. Hydrogen peroxide, chloric and chromic acids do not give the reaction.[48] Pyrogallol dimethyl ether is recommended as a very delicate test for chromic acid, ferric salts, and nitrites. Chloroform extracts the yellow colouring matter.[49] It has been stated that arsenic acid may be detected in presence of phosphoric acid by the white precipitate which results when a solution of ammonium molybdate and nitrate is added to that to be tested which must contain acetic acid.[50]

Some useful observations have been made on the detection and separation of the heavy metals that are not precipitated by hydrogen sulphide in acid solution. Thus a scheme for their separation has been devised,[51] whilst it has been shown that on addition of ammonium perchlorate to ammoniacal solutions of cobalt, nickel, manganese, and cadmium salts, these metals are completely precipitated as perchlorates of the metallic ammines.[52] It has been stated that potassium cobalticyanide gives, in presence of sulphurous acid, a red precipitate with zinc salts and a yellow precipitate (which turns green on heating) with nickel salts, both precipitates being soluble in an excess of the reagent. The nickel precipitate is bleached by tartaric acid.[53] The rose colour of a solution of cobalt naphthenate in benzene has been suggested as a test for cobalt in presence of nickel, whilst it has been stated that paper coloured with this solution is bleached when moistened with dilute hydrogen peroxide.[54]

When sodium cobaltinitrite is added to a faintly acid solution of

46 *Zeitsch. anorg. Chem.*, 1900, **23**, 236 ; *A.*, 1900, ii, 436.
47 *J. Russ. Phys. Chem. Soc.*, 1909, **41**, 1301 ; *A.*, ii, 154.
48 J. Schmidt and H. Lumpp, *Ber.*, 1910, **43**, 432, 794 ; *A.*, i, 313, ii, 450.
49 J. Meyerfeld, *Chem. Zeit.*, 1910, **34**, 948 ; *A.*, ii, 901.
50 G. Maderna, *Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 68 ; *A.*, ii, 896.
51 J. Petersen, *Zeitsch. anal. Chem.*, 1910, **67**, 253 ; *A.*, ii, 654.
52 R. Salvadori, *Gazzetta*, 1910, **40**, ii, 19 ; *A.*, ii, 1002.
53 E. P. Alvarez, *Ann. Chim. anal.*, 1910, **15**, 129 ; *A.*, ii, 454.
54 K. W. Charitschkoff, *Chem. Zeit.*, 1910, **34**, 50, 479 ; *A.*, ii, 238, 549.

a thallium salt, a red, crystalline precipitate of the composition $Th_3Co(NO_2)_6$ is formed. The reaction is said to be delicate, and when employed conversely serves for the detection of cobalt in presence of nickel.[55]

A very sensitive reagent for copper is said to be a solution of 1 : 2-diaminoanthraquinone-3-sulphonic acid in sodium hydroxide. A blue coloration is produced.[56]

J. Piccard [57] having suggested that H. J. H. Fenton's colour reaction with quadrivalent titanium and dihydroxymaleic acid may be due to tervalent titanium, Fenton has since shown [58] that the colorations produced by quadrivalent and tervalent titanium are distinct.

O. F. Kirby [59] recommends asbestos threads soaked in phosphoric acid, dried, rolled together and ignited, for flame coloration tests, borax beads, etc.

Quantitative.

Non-Metals.—The suggestion has been made to estimate free halogens by shaking solutions containing them with a known weight of electrolytically deposited silver in an atmosphere of hydrogen and determining the increase in weight,[60] and it is obvious that the method may be used for the indirect estimation of a large number of substances.[61] The method of estimating iodide in presence of bromide or chloride—oxidation with permanganate, extraction of the iodine with carbon tetrachloride, and titration with thiosulphate—originally proposed by Sammet,[62] has been shown to give results accurate to within 0·1 per cent.[63]

For the estimation of small quantities of nitrates, say a few centigrams, it has been suggested to apply the Pelouze reaction—action of an acidified solution of ferrous chloride on a nitrate—and for the measurement of the nitric oxide evolved in this reaction an apparatus of the Schultze-Tiemann type has been devised by A. T. Davenport.[64]

Several papers have been published during the year dealing with

[55] S. Tanatar and S. Petroff, *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 94 ; *A.*, ii, 350.
[56] R. Uhlenhuth, *Chem. Zeit.*, 1910, **34**, 887 ; *A.*, ii, 898.
[57] *Ber.*, 1909, **42**, 4341 ; *A.*, i, 67.
[58] *Ibid.*, 1910, **43**, 267 ; *A.*, ii, 244.
[59] *Chem. News*, 1910, **101**, 170 ; *A.*, ii, 445.
[60] F. A. Gooch and C. C. Perkins, *Amer. J. Sci.*, 1909, [iv], **28**, 33 ; *A.*, 1909, ii, 932 ; and C. C. Perkins, *ibid.*, 1910, [iv], **29**, 338 ; *A.*, ii, 542.
[61] Compare *ibid.*, 1910, [iv], **29**, 540 ; *A.*, ii, 659.
[62] *Zeitsch. physikal. Chem.*, 1905, **53**, 684 ; *A.*, 1906, ii, 153.
[63] W. C. Bray and G. M. Mackay, *J. Amer. Chem. Soc.*, 1910, **32**, 1193 ; *A.*, ii, 996.
[64] *J. Amer. Chem. Soc.*, 1910, **32**, 1237 ; *A.*, ii, 998.

the estimation of phosphoric acid volumetrically, but since the methods proposed are in some cases more complicated and apparently less accurate than those now in use, they need not be discussed. An interesting, lengthy, and important review on magnesium ammonium phosphate, and the best conditions for its precipitation in analysis, is published by K. Bube.[65]

The benzidine method of estimating sulphuric acid has now been proved to be one of considerable utility by numerous observers, and some useful details of its application to the analysis of pyrites and to the estimation of sulphuric acid in presence of chromic salts and chromic acid are given by G. von Knorre.[66] It is well known to chemists that the assay of fuming sulphuric acid ("oleum") is attended with some difficulty, and the simple and rapid method devised by H. Howard,[67] which is specially suitable for works' requirements, is therefore welcome. It depends on the measurement of the heat evolved when a known weight of the sample is diluted with sulphuric acid of 92 per cent. concentration.

The fact that arsenic may be distilled rapidly from its solutions in one operation in presence of hydrochloric and hydrobromic acids and a salt of hydrazine is a useful addition to our knowledge.[68] In the estimation of small quantities of arsenic by the Marsh-Berzelius method, it was shown by Chapman and Law in 1906 that the addition of a salt of cadmium to the generating flask (whereby metallic cadmium is deposited on the zinc) increases the sensitiveness of the zinc. W. D. Harkins[69] finds that the same effect is produced by the salts of all metals of high excess potential, for example, tin, lead, and bismuth.

A method of estimating cyanides by titration with a nickel salt in neutral solution has been proposed. The end point is indicated by a turbidity due to the precipitation of nickel cyanide. It gives fairly accurate results, and may be used in presence of halides and thiocyanates.[70] It will be remembered that H. G. Colman[71] recommended the Feld method of estimating ferrocyanides. F. W. Skirrow[72] has brought forward experimental evidence that the results are 3 to 4 per cent. too low. This has since been refuted by Colman,[73] who shows that there is a loss of hydrogen cyanide,

[65] *Zeitsch. anal. Chem.*, 1910, **49**, 525; *A.*, ii, 804.
[66] *Chem. Zeit.*, 1910, **34**, 405; *A.*, ii, 545.
[67] *J. Soc. Chem. Ind.*, 1910, **29**, 3; *A.*, ii, 239.
[68] P. Jannasch and T. Seidel, *Ber.*, 1910, **43**, 1218; *A.*, ii, 546.
[69] *J. Amer. Chem. Soc.*, 1910, **32**, 518; *A.*, ii, 451.
[70] H. Grossmann and L. Hölter, *Chem. Zeit.*, 1910, **34**, 182; *A.*, ii, 349.
[71] *Analyst*, 1908, **33**, 261; *Ann. Report*, 1908, 201.
[72] *J. Soc. Chem. Ind.*, 1910, **29**, 319; *A.*, ii, 361.
[73] *Analyst*, 1910, **35**, 295; *A.*, ii, 761.

although only of 0·6 per cent., if the boiling with magnesium chloride be protracted; not, however, if his conditions [74] be adhered to. The loss during the conversion of the ferrocyanide into mercuric cyanide is also shown to be less than stated by Skirrow. J. L. Foucar [75] corroborates Colman's statements.

Metals.—Volumetric methods of estimating lead and zinc, depending on titration with potassium cyanide, are described by E. Rupp,[76] whilst H. Grossmann and L. Hölter [77] deal with the estimation of zinc by titration with potassium cyanide in presence of ammonium chloride, potassium iodide, and silver nitrate. A tintometric method for the approximate estimation of small quantities of lead has been devised by A. G. Vernon Harcourt.[78] The proposal to estimate mercury in presence of silver and of the two metals together by titration with thiocyanate appears worthy of attention,[79] as does also the suggestion to estimate small quantities of silver by coloration produced (colloidal silver) when a solution is heated with sodium hydroxide and a carbohydrate or glycerol.[80]

H. F. V. Little and E. Cahen [81] show that Benkert and Smith's method of separating bismuth from lead, double precipitation as bismuth formate,[82] gives good results.

Last year, O. Baudisch [83] showed that nitrosophenylhydroxylamine, known as "cupferron," precipitates iron and copper quantitatively, and he gave a number of instances of its use in the analysis of ores. His results have been confirmed by H. Biltz and O. Hödtke,[84] who give some further useful details. Silver, mercury, lead, and tin are said to be precipitated quantitatively by "cupferron." [85]

A method for the separation of antimony and tin was described last year by L. W. McCay,[86] and further details are now published by the same author.[87] According to W. Plato,[88] antimony and tin may be separated by distillation. To a solution containing the two metals, sufficient concentrated sulphuric acid is added to raise

74 *Loc. cit.* 75 *Ibid.*, 300.
76 *Chem. Zeit.*, 1910, **34**, 121; *A.*, ii, 243.
77 *Ibid.*, 181; *A.*, ii, 349.
78 *Trans.*, 1910, **97**, 841.
79 E. Rupp and F. Lehmann, *Chem. Zeit.*, 1910, **34**, 229; *A.*, ii, 350.
80 G. S. Whitby, *Zeitsch. anorg. Chem.*, 1910, **67**, 62; *A.*, ii, 654.
81 *Analyst*, 1910, **35**, 301; *A.*, ii, 755.
82 *J. Amer. Chem. Soc.*, 1896, **18**, 1055; *A.*, 1897, ii, 755.
83 *Chem. Zeit.*, 1909, **33**, 1298; *A.*, ii, 76.
84 *Zeitsch. anorg. Chem.*, 1910, **66**, 426; *A.*, ii, 550.
85 Compare J. Hanuš and A. Soukup, *ibid.*, **68**, 52; *A.*, ii, 899.
86 *Ann. Report*, 1909, 143.
87 *J. Amer. Chem. Soc.*, 1910, **32**, 124; *A.*, ii, 1003.
88 *Zeitsch. anorg. Chem.*, 1910, **68**, 26; *A.*, ii, 903.

the boiling to 155—165°, and distillation commenced in a current of carbon dioxide, when the antimony passes over. More sulphuric and hydrochloric acids are then added, together with bromine, and the distillation continued in a current of sulphur dioxide, the tin passing over as tetrachloride at a temperature of 180—190°. H. Reckleben and A. Güttisch[89] point out that the hydrides of antimony and arsenic behave similarly towards silver nitrate solution. They state that the deposited silver cannot be taken as a measure of the antimony, as it is invariably contaminated with antimony oxide; further, that the complete oxidation of antimony hydride to antimonic acid is only possible if a convenient solvent be present. Their observation is worthy of note that alkali and alkali earths decompose antimony hydride more readily than arsenic hydride.

H. E. Palmer[90] has applied the principle of oxidation with potassium ferricyanide in alkaline solution and titration of the resulting ferrocyanide with permanganate to the estimation of arsenic, antimony, tin, vanadium, and chromium, and in this connexion attention may be called to two papers in which the titration of ferrocyanide with permanganate is discussed.[91]

Several papers dealing with the estimation of nickel and cobalt demand notice. In the first place, E. L. Rhead[92] has submitted several methods for the estimation of nickel in nickel steel to a critical investigation, and he concludes that the Brunck-Ivanicki method (precipitation with dimethylglyoxime) is the most accurate and rapid, the separation of iron being effected by basic precipitation. H. Grossmann and B. Schück, criticising Rhead,[93] claim as great accuracy for their dicyanodiamidine method.[94] They point out, however, that titration with potassium cyanide is just as accurate, and far more rapid.[95]

For the estimation of both nickel and cobalt, E. Rupp and F. Pfenning[96] describe a method of direct titration with potassium cyanide. The assay liquid (neutral to methyl-orange) is run into a measured volume of *N*/2-potassium cyanide solution. In the case of nickel, the cyanide may be run into the assay liquid. The end points correspond with the ratios Co : 5KCN and N : 4KCN.[97] A method for the estimation of nickel and cobalt, which is claimed

[89] *Zeitsch. anal. Chem.*, 1910, **49**, 73; *A.*, ii, 352.

[90] *Amer. J. Sci.*, 1910, [iv], **29**, 399, **30**, 141; *A.*, ii, 546, 902.

[91] W. Mecklenburg, *Zeitsch. anorg. Chem.*, 1910, **67**, 322; *A.*, ii, 761; E. Müller and O. Diefenthäler, *ibid.*, 418; *A.*, ii, 910.

[92] *Analyst*, 1910, **35**, 97; *A.*, ii, 352.

[93] *Ibid.*, 247; *A.*, ii, 658.

[94] *Ann. Report*, 1907, 205.

[95] Compare Campbell and Arthur, *ibid.*, 1908, 191.

[96] *Chem. Zeit.*, 1910, **34**, 322; *A.*, ii, 458.

[97] Compare, however, H. Grossmann, *ibid.*, 673.

to be particularly adapted for the estimation of nickel in steel, has been devised by G. S. Jamieson.[98] It depends on titration with potassium ferrocyanide, and from the results quoted it appears very accurate.

The precipitation of iron, aluminium, and chromium as basic formates has been recommended on the ground that the precipitates filter better than the acetates.[99] When titrating ferrous salts by permanganate in presence of hydrochloric acid, it is shown that accurate results can be obtained if phosphoric acid be added.[1] When silicates are decomposed by sulphuric and hydrofluoric acids, the excess of the latter should preferably be converted into hydrofluosilicic acid by addition of pure silica, and the ferrous iron titrated with permanganate.[2]

Volhard's well-known permanganate method for the estimation of manganese has been studied by W. M. Fischer,[2a] who has suggested the addition of glacial acetic acid to the boiling liquid just before the titration is completed, which causes the precipitate to subside. E. Cahen and H. F. V. Little[2b] show that the liquid should be below boiling point when the acetic acid is added. The experimental data which they bring forward goes to prove that the accuracy of the method for the analysis of such substances as ferromanganese and pyrolusite compares favourably with that of gravimetric and volumetric methods in general use. Two modifications of the Volhard-Wolff method of estimating manganese are described by E. Deiss.[3] It has been found that a solution of manganese in sulphuric acid is oxidised to the quadrivalent state by sodium bismuthate, and a method for the estimation of manganese based on this fact has been described by F. J. Metzger and R. F. McCrackan.[4]

The difficulty of separating calcium and magnesium by the oxalate method when the magnesium largely predominates is well known, and E. Murmann[5] has suggested dissolving the mixed chlorides in alcohol and precipitating the calcium from this solution as sulphate.

The method for the estimation of alkalis originally devised by

[98] *J. Amer. Chem. Soc.*, 1910, **32**, 757 ; *A.*, ii, 658.

[99] O. F. Tower, *ibid.*, 953 ; *A.*, ii, 900.

[1] G. J. Hough, *ibid.*, 539 ; *A.*, ii, 457.

[2] J. Fromme, *Tsch. Min. Mitt.*, 1909, **28**, 329 ; *A.*, ii, 351.

[2a] *Zeitsch. anal. Chem.*, 1909, **48**, 751 ; *A.*, ii, 76.

[2b] *Analyst*, 1911, **36**, 43.

[3] *Chem. Zeit.*, 1910, **34**, 237 ; *A.*, ii, 351 ; compare E. Donath, *ibid.*, 437 ; *A.*, ii, 550.

[4] *J. Amer. Chem. Soc.*, 1910, **32**, 1250 ; *A.*, ii, 1000.

[5] *Zeitsch. anal. Chem.*, 1910, **49**, 688 ; *A.*, ii, 897.

Lawrence Smith [6] has been studied by T. Döring,[7] who gives some valuable hints concerning it. H. Roemer [8] has published a useful summary of the methods for the analysis of potash salts (native) adopted by the International Congress of Applied Chemistry at Berlin, 1903. The accuracy of the cobaltinitrite method of estimating potassium volumetrically originally devised by Adie and Wood, and further developed by Drushel,[9] has been doubted by certain observers; but a modification has now been devised which, on the evidence of several chemists, gives results which are sometimes, although rarely, 1 per cent. too high.[10] W. C. Ball [11] has developed his method of estimating sodium and cæsium as sodium cæsium bismuthinitrite,[12] and his results are highly satisfactory. None of the positive ions commonly associated with sodium, for example, calcium, magnesium, lithium, interferes. Ammonium chloride should not be present in concentration above $N/5$, and phosphate, if it occur in more than traces, must be removed. J. C. H. Mingaye [13] has made a study of several methods of estimating thorium in monazite, and one of his conclusions is that Haber's method,[14] precipitation as basic acetate, is rapid and sufficiently accurate. For this purpose, R. J. Meyer and M. Speter [15] make use of the fact that thorium iodate is insoluble in nitric acid provided that an alkali be present in excess. For the estimation of cerium in cerite or monazite, F. J. Metzger and M. Heidelberger [16] apply the method previously described,[17] namely, oxidation with sodium bismuthate, reduction of the ceric salt with ferrous sulphate, and titration of the excess of the latter with permanganate.

A. Gemmell [18] has improved H. D. Newton's volumetric method of estimating titanium. He employs an alloy of aluminium and magnesium ("magnalium"), or preferably a zinc-aluminium alloy, as reducing agent. The latter alloy reduces ferric salts immediately at 40—50°, but thirty to forty-five minutes are required for the reduction of titanium salts. By taking advantage of these facts,

[6] *Amer. J. Sci.*, 1871, [iii], **1**, 296.
[7] *Zeitsch. anal. Chem.*, 1910, **49**, 158; *A.*, ii, 348.
[8] *Chem. News*, 1910, **101**, 54; *A.*, ii, 347.
[9] *Ann. Report*, 1908, 193.
[10] O. M. Shedd, *J. Ind. Eng. Chem.*, 1910, **2**, 379.
[11] *Trans.*, 1910, **97**, 1408.
[12] *Ann. Report*, 1909, 146.
[13] *Records Geol. Survey, N. S. Wales*, 1909, **8**, 276; *A.*, ii, 78.
[14] *Monatsh.*, 1897, **18**, 687; *A.*, 1898, ii, 295.
[15] *Chem. Zeit.*, 1910, **34**, 306; *A.*, ii, 459.
[16] *J. Amer. Chem. Soc.*, 1910, **32**, 642; *A.*, ii, 656.
[17] *Ann. Report*, 1909, 146.
[18] *Analyst*, 1910, **35**, 198; *A.*, ii, 899.

he estimates iron and titanium in a mineral by double titration with permanganate. O. L. Barnebey and R. M. Isham[19] describe a rapid and accurate method of estimating titanium in presence of iron. The latter metal is extracted by ether as ferric chloride, and the titanium is precipitated as dioxide in acetic acid solution. Traces of titanium, after separating the iron in the manner described, may be estimated tintometrically with hydrogen peroxide. P. E. Browning and H. E. Palmer[20] estimate vanadium as silver metavanadate by addition of silver nitrate to a neutral solution. The chemistry of osmium and its estimation is dealt with in a paper by O. Ruff and F. Bornemann.[21] Instead of separating niobium and tantalum, the oxides of the two metals may be weighed together, and their relative amounts calculated from the specific gravity of the mixture.[22]

It is shown by L. Rössler[23] that gold may be precipitated from its solutions as metal by addition of alkaline hydrogen peroxide. J. C. H. Mingaye[24] states that as little as 0·06 gram per ton of platinum in alluvial deposits may be estimated tintometrically with stannous chloride.

The remarkable accuracy attained at the Royal Mint in the assay of gold bullion is shown by J. Phelps,[25] who arrives at the conclusion that the error for the mean of, say, 20 assays made with the greatest care should not exceed 0·01 per 1000.

The iodoeosin method of measuring the alkalinity of glass was first described by F. Mylius in 1889, and since then numerous papers on its application have been published by the same author and his collaborators. It has been found that the tendency of glass to disintegrate ("weathering" tendency), either by the action of liquid reagents or by exposure to the air, as measured by this method, enables glasses to be classified into three types: (*a*) Light glasses which show little, if any, increase in alkalinity after "weathering"; (*b*) light glasses (used with due protection for optical purposes), which show a very large increase in alkalinity after weathering; (*c*) heavy optical glasses which show a decrease in alkalinity after "weathering."[26]

19 *J. Amer. Chem. Soc.*, 1910, **32**, 957; *A.*, ii, 901.
20 *Amer. J. Sci.*, 1910, [iv], **30**, 220; *A.*, ii, 902.
21 *Zeitsch. anorg. Chem.*, 1910, **65**, 429; *A.*, ii, 305.
22 H. W. Foote and R. W. Langley, *Amer. J. Sci.*, 1910, [iv], **30**, 393; *A.*, 1911, ii, 71.
23 *Zeitsch. anal. Chem.*, 1910, **49**, 739; *A.*, ii, 1115.
24 *Record Geol. Survey, N. S. Wales*, 1909, **8**, 276; *A.*, ii, 78.
25 *Trans.*, 1910, **97**, 1272.
26 *Zeitsch. anorg. Chem.*, 1910, **67**, 200; *Ber.*, 1910, **43**, 2130; *A.*, ii, 656.

Electrochemical Analysis.

A great deal of useful work has been done during the year on this branch of analytical chemistry. In the first place, a report has been issued by the Electro-Analysis Committee of the British Association for the Advancement of Science. In it the work of F. M. Perkin and W. E. Hughes, and of H. J. S. Sand is discussed. The latter chemist, it is stated, has obtained satisfactory results for copper with a cathode of silver, and for zinc with a cathode of nickel. It has been found that chlorides exert a retarding influence on the deposition of copper, owing to the formation of derivatives of cuprous chloride, from which the copper is only deposited at a high potential. Alloys containing copper, antimony, and tin have, it is stated, been satisfactorily analysed. When lead is present, it may be deposited with the tin, but means of separating the two when this occurs have been found. A review on the progress of electro-analysis has been published by A. Stähler,[27] whilst another review has been published by the same chemist, in which special reference is made to rapid methods with rotating electrodes and solutions.[28] F. Foerster [28a] deals similarly with the work carried out during the year 1909.

Last year, it will be remembered that J. Stoddard [29] showed that several metals can be deposited rapidly and completely with the use of stationary electrodes and *strong* currents, the latter causing the solution to be agitated by the vigorous gas evolution. He employed a platinum gauze cylindrical cathode and a mercury cathode. The experiments with the platinum cathode have been repeated by T. S. Price and T. C. Humphreys,[30] who find that for rapid electro-analysis stationary electrodes are less trustworthy than rotating electrodes. On the other hand, R. C. Benner [31] has repeated Stoddard's experiments, using a mercury cathode, and his results show that with copper, silver, cadmium, and bismuth, the method is almost as rapid as when a rotating anode is used, and that the results are as accurate as those obtained by other methods in which mercury is employed as a cathode.[32] F. M. Perkin and W. E. Hughes [33] describe various forms of rotating electrodes for the rapid deposition of metals. They recommend a *rotating* anode, consisting of a closely wound spiral of iridio-platinum wire and a

[27] *Fortschr. Chem. Phys. und phys. Chem.*, 1910, **2**, 215.
[28] *Zeitsch. Elektrochem.*, 1910, **16**, 551.
[28a] *Ibid.*, 826.
[29] *Ann. Report*, 1909, 151.
[30] *J. Soc. Chem. Ind.*, 1910, **29**, 307 ; *A.*, ii, 446.
[31] *J. Amer. Chem. Soc.*, 1910, **32**, 1231 ; *A.*, ii, 999.
[32] Compare also W. S. Kimley, *ibid.*, 637 ; *A.*, ii, 654.
[33] *Trans. Faraday Soc.*, 1910, **6**, 14 ; *Chem. News*, 1910, **101**, 52 ; *A.*, ii, 898.

cylindrical *stationary* cathode of platinum gauze of fine mesh. Some important new apparatus for the rapid estimation of metals was described by H. J. S. Sand and W. M. Smalley at a meeting of the Faraday Society on December 10th. The electrodes are similar to those designed by Sand in 1907 and 1908, and the anode requires only about 5 grams of platinum.

H. J. S. Sand [34] gives some further details of his method of estimating lead as dioxide.[35] Other facts concerning the method are published by R. C. Benner,[36] who confirms the accuracy of Sand's results. B. Pasztor [37] deals with the rapid estimation of tin with varying strengths of current, different temperatures, and different electrolytes. A very useful paper on the conditions affecting the electrolytic estimation of copper is published by W. C. Blasdale and W. Cruess.[38]

It has been found that high results are invariably obtained in the electrolytic estimation of zinc,[39] and that this is due to the deposition of hydroxide along with metallic zinc.[40] The advantage of employing certain organic electrolytes in the estimation of cadmium has been pointed out by the Misses M. E. Holmes and M. V. Dover.[41] A rotating anode is employed with a current below one ampere. Cadmium formate in presence of calcium acetate and lactate gave good results, whereas the acetate and lactate electrolytes alone were less successful. Useful data are given on the electrolytic separation of several metals by J. H. Buckmaster and E. F. Smith.[42] A paper has appeared on the estimation of tin in brass and other alloys,[43] and another on the estimation of tin in white metal.[44] Miss L. G. Kollock and E. F. Smith [45] show that from a solution containing a little free acid and 0·2 gram of indium sulphate, metallic indium may be rapidly and completely deposited with the use of a mercury cathode in conjunction with a rotating anode. The total dilution is 10 c.c.; the current 2—4 amperes at an E.M.F. of 7·5 to 6·5 volts.

Last year it was shown by F. A. Gooch and H. L. Read [46] that

[34] *Trans. Faraday Soc.*, 1910, **5**, 207; *A.*, ii, 456.
[35] *Ann. Report*, 1909, 151.
[36] *J. Ind. Eng. Chem.*, 1910, **2**, 348.
[37] *Elektrochem. Zeit.*, 1910, **16**, 281; *A.*, ii, 459.
[38] *J. Amer. Chem. Soc.*, 1910, **32**, 1264; *A.*, ii, 1112.
[39] E. B. Spear, E. E. Wells, and B. Dyer, *ibid.*, 530; *A.*, ii, 455.
[40] E. B. Spear, *ibid.*, 533; *A.*, ii, 455.
[41] *Ibid.*, 1251; *A.*, ii, 1111.
[42] *Ibid.*, 1471; *A.*, ii, 1112.
[43] E. Schürmann and H. Arnold, *Mitt. K. Materialprüfungsamt.*, 1909, **27**, 470; *A.*, ii, 549.
[44] E. Schürmann, *Chem. Zeit.*, 1910, **34**, 1117; *A.*, ii, 1115.
[45] *J. Amer. Chem. Soc.*, 1910, **32**, 1248; *A.*, ii, 1000.
[46] *Amer. J. Sci.*, 1909, [iv], **28**, 544; *A.*, ii, 67.

the estimation of chlorine in hydrochloric acid with the use of a silver anode gives low results, owing to the passage of silver from the anode to the cathode, and to the formation of hypochlorous acid. These chemists employed a platinum cathode, and their results have been confirmed by J. S. Goldbaum and E. F. Smith,[47] who find, however, that with a rotating silver anode and a mercury cathode a high degree of accuracy may be attained.

Organic Chemistry.

Qualitative.—There are but few papers in this category which demand notice. In the course of his studies on the photochemical synthesis of formaldehyde in green plants, S. B. Schryver[48] has increased the sensitiveness of Rimini's phenylhydrazine test for formaldehyde. He shows that it is specific, and that the intensity of the coloration gives an indication of the actual quantity. Some useful suggestions are made by G. Denigès[49] on the detection of traces of formaldehyde by Schiff's reagent. He uses this reagent for the detection of methyl alcohol in presence of ethyl alcohol, the mixture being first treated with permanganate and the excess of the latter destroyed.[50]

For the detection of trichloroacetic acid by the formation of chloroform, R. Stollé[51] suggests heating with antipyrine instead of with potassium hydroxide or aniline. The former causes the evolution of chloroform from chloral hydrate, whilst the odour of aniline might mask that of chloroform.

In 1891, Janovsky showed that sodio- or potassio-acetone gives colour reactions with aromatic dinitro-compounds, and in the following year von Bitto observed that the same reagent might be used as a test for aldehydes and ketones. As indicating the mechanism of the reaction, F. Reitzenstein and G. Stamm[52] bring forward evidence that the compound formed in the case of 1-chloro-2:4-dinitrobenzene is probably the condensation derivative, $CH_2{:}CMe{\cdot}O{\cdot}C_6H_3(NO_2)_2$. A tabulated list is given of the colorations obtained by several dinitro-compounds, aldehydes, and ketones by Janovsky's reagent.

Scatole may, it is said, be distinguished from tryptophan, indole, or 2-methylindole by the fact that when a solution even as dilute as 1 in 5,000,000 is mixed with 3 drops of methyl alcohol and 3 drops

47 *J. Amer. Chem. Soc.*, 1910, **32**, 1468; *A.*, ii, 1107.
48 *Proc. Roy. Soc.*, 1910, B, **82**, 226; *A.*, ii, 334.
49 *Compt. rend.*, 1910, **150**, 529; *A.*, ii, 357.
50 *Ibid.*, 832; *A.*, ii, 461.
51 *Ber. Deut. pharm. Ges.*, 1910, **20**, 371; *A.*, ii, 1119.
52 *J. pr. Chem.*, 1910, [ii], **81**, 167; *A.*, ii, 358.

of sulphuric acid, a violet-red coloration is produced.[53] Several colour reactions given by dried egg albumin and different reagents are described by C. Reichard.[54]

W. Harrison[55] has drawn the conclusion that the blue coloration of iodine with starch is merely a colloidal solution of iodine, the starch acting as a protective colloid. His further conclusion that the dextrins and "starch celluloses" (?) are all different colloidal states of starch and not chemically different compounds is one which does not appear to be supported by any evidence.

Quantitative.

Ultimate Analysis.—It is well known that the estimation of carbon and nitrogen in anthracene derivatives and other complex aromatic compounds of high molecular weight is attended with difficulty. The subject is dealt with by R. Scholl,[56] who recommends Dennstedt's methods. For nitrogen, he prefers a method which consists in placing about 1 gram of potassium chlorate in a boat in the fore part of the tube. After the main portion of the nitrogen has been evolved, this chlorate is ignited until the copper spiral commences to blacken. In these circumstances, no oxygen need gain access to the azotometer. The allegation of H. Weil,[57] that lead peroxide retains carbon dioxide, has been shown by M. Dennstedt and F. Hassler[58] to be unfounded; but they point out that the commercial product frequently contains organic matter. The estimation of carbon and hydrogen in the calorimetric bomb is dealt with by H. L. Higgins and Miss A. Johnson,[59] and also by E. Grafe.[60] J. Marcusson and H. Döscher[61] describe a modification of the Hempel-Graefe method of estimating sulphur,[62] by means of which the halogens may also be estimated.

Commercial Products.

Foods and Food Materials.—In 1898, J. L. Baker and the writer recommended the use of invertase instead of acid for inverting sucrose in commercial products when carrying out the Clerget method, and this has been further worked out by C. S. Hudson.[63]

53 T. Sasaki, *Biochem. Zeitsch.*, 1910, **23**, 402; *A.*, ii, 166.
54 *Pharm. Zeit.*, 1910, **55**, 158; *A.*, ii, 363.
55 *Proc.*, 1910, **26**, 252.
56 *Ber.*, 1910, **43**, 342 [footnote]; *A.*, ii, 285.
57 *Ibid.*, 149; *A.*, ii, 242. 58 *Ibid.*, 1196; *A.*, ii, 547.
59 *J. Amer. Chem. Soc.*, 1910, **32**, 347; *A.*, ii, 460.
60 *Biochem. Zeitsch.*, 1910, **24**, 277; *A.*, ii, 460.
61 *Chem. Zeit.*, 1910, **34**, 417; *A.*, ii, 543.
62 *Zeitsch. angew. Chem.*, 1904, **17**, 616; *A.*, 1904, ii, 514.
63 *U. S. Depart. of Agric.*, *Bureau of Chemistry*, Circular No. 50.

In a paper read before the London Section of the Society of Chemical Industry on January 2nd, 1911, further details of this method have been worked out by J. P. Ogilvie, whereby its accuracy has been increased. In many respects it is to be preferred to the acid inversion process. N. Deerr[64] deals with the influence of the volume of the lead acetate precipitate in the estimation of sucrose in molasses by the Clerget process.[65] For the estimation of sucrose in presence of lactose, glucose, or fructose, it has been suggested to heat the mixture with alkaline hydrogen peroxide and a little manganese dioxide, whereby it is said that the reducing and optical powers of the two latter sugars are destroyed, whilst sucrose is not affected.[66] Maltose must not be present. This method, and that of heating with dilute sodium hydroxide to destroy reducing sugars in presence of sucrose,[67] even if trustworthy, which is open to doubt, have no advantage over existing methods. It has been proposed to estimate lactose and sucrose in mixtures by taking advantage of the fact that the Bulgarian (lactic) organism converts lactose into lactic acid, whilst it is without action on sucrose.[68] It has also been shown that lactose may be estimated in admixture with the commonly occurring fermentable sugars by fermenting a solution of the mixture with ordinary *Saccharomyces cerevisiae*, the reducing power of the solution after fermentation being due entirely to lactose.[69] A similar fermentation method of estimating lactose in presence of other sugars has been used by the writer with satisfactory results. For the detection of artificial invert sugar in honey, Fiehe's resorcinol test, depending on the presence of β-hydroxy-δ-methylfurfuraldehyde, which is said to be invariably present in artificial invert sugar,[70] has been confirmed.[71] Less value must be attached to tests for detecting natural honey, since they do not of necessity show the absence of the artificial product in mixtures. The novel suggestion has been made of distinguishing natural honey by a physiological (serum) test,[72] and it has also been proposed to characterise natural honey by determining its catalytic and diastatic powers,[73] a method which may perhaps permit of

[64] *Bull.*, 31, 1910; *Agric. and Chem. Series: Expt. Station, Hawaiian Sugar Planters' Assoc.*

[65] Compare L. Eynon, *Ann. Report*, 1909, 158.

[66] P. Lemeland, *Ann. Chim. anal.*, 1910, **15**, 415; *A.*, ii, 1007.

[67] A. Jolles, *Zeitsch. Nahr. Genussm.*, 1910, **20**, 631; *A.*, 1911, ii, 74.

[68] G. Bertrand and F. Ducháček, *Compt. rend.*, 1909, **148**, 1338; *A.*, 1909, i, 623; L. Margaillan, *ibid.*, 1910, **150**, 45; *A.*, ii, 163.

[69] J. L. Baker and H. F. E. Hulton, *Analyst*, 1910, **35**, 512; *A.*, 1911, ii, 74.

[70] *Zeitsch. Nahr. Genussm.*, 1908, **16**, 75.

[71] Witte, *ibid.*, 1909, 625; F. Reinhardt, *ibid.*, 1910, **20**, 113; and F. Muttelet, *Ann. Falsif.*, 1910, **3**, 206; *A.*, ii, 660.

[72] J. Langer, *Arch. Hygiene*, 1910, **71**, 308.

[73] A. Auzinger, *Zeitsch. Nahr. Genussm.*, 1910, **19**, 65.

quantitative expression. It is worthy of note that the presence of formaldehyde in sugar-cane juice and in sugar house products has been established.[74] The suggestion to employ a solution of phenylhydrazine in sulphurous acid instead of the base itself on the ground that it yields purer osazones with the sugars appears well worthy of the attention of analytical chemists.[75]

Now that it has been shown by Chapman[76] that the Jaffé reaction between creatinine and picric acid is simply one of reduction of the latter, it has become very important actually to establish the presence of creatinine in the case of assays carried out by the Jaffé method, and some useful data for the isolation of creatinine from meat extracts have been published.[77]

R. R. Tatlock and R. T. Thompson[78] have communicated a useful paper giving the composition of coffee of various origin and chicory. They suggest calculating the percentage of chicory in mixtures of that substance with coffee from the percentages of caffeine and ash. In the writer's opinion, the data brought forward are insufficient.

Attention has been called to the fact that salicylic acid is a normal constituent of fruits and wines. The amount normally present in wines is said to be 0·001 gram per litre.[79] An important paper on the estimation of salicylic acid in jams, etc., by a modification of Harry and Mummery's method has appeared.[80] A substance resembling Brandt's maltol has been discovered in baked bread and biscuits, and, like maltol, it gives a colour reaction with ferric salts, so that it is liable to be mistaken for salicylic acid.[81]

Miss M. E. Pennington and A. D. Greenlee[82] have applied a modification of Folin's method to the estimation of loosely-combined nitrogen in flesh. In the case of fowls, this percentage of nitrogen is shown to increase even when kept in cold store.

Drugs, Alkaloids, Etc.—For the estimation of starch in mustard, H. Kreis[83] recommends a modification of Mayrhofer's method of isolating the starch and weighing it as such.

Certain modifications in the Codex method of estimating caffeine

[74] P. A. Yoder and W. G. Taggart, *J. Ind. Eng. Chem.*, 1910, No. 6; *Chem. News*, 1910, **102**, 26.

[75] J. Böeseken, *Chem. Weekblad*, 1910, **7**, 934; *A.*, ii, 1118.

[76] *Ann. Report*, 1909, 159.

[77] K. Micko, *Zeitsch. Nahr. Genussm.*, 1910, **19**, 426; *A.*, ii, 557.

[78] *J. Soc. Chem. Ind.*, 1910, **29**, 138.

[79] H. Pellet, *Ann. Chim. anal.*, 1910, **15**, 302; *A.*, ii, 906.

[80] *Zeitsch. Nahr. Genussm.*, 1910, **20**, 63; *A.*, ii, 906.

[81] A. Backe, *Compt. rend.*, 1910, **150**, 540; *A.*, i, 225.

[82] *J. Amer. Chem. Soc.*, 1910, **32**, 561; *A.*, ii, 449.

[83] *Chem. Zeit.*, 1910, **34**, 1021.

in cola have been suggested by Desvignes.[84] E. Bierling, K. Pape, and A. Viehöver [85] have investigated the methods which have been proposed for the evaluation of coca leaves, and make some definite recommendations.

P. van der Wielen [86] describes methods for the estimation of morphine, narcotine, and codeine in opium and its galenical preparations. A critical review of the methods of testing digitalis preparations is published by C. Focke,[87] and he has further developed the physiological method of testing both digitalis and strophanthus preparations.[88] J. Burmann, jun.,[89] brings forward evidence that the so-called physiological titration method is inferior to the chemical methods for determining the value of digitalis preparations.

The titration of alkaloids with different indicators is dealt with by E. Runne,[90] whilst the difficulties attending this are pointed out by E. Elvove.[91] Elvove suggests titrating the hydrochlorides by Volhard's method after previously washing them with alcohol.

F. H. Carr and W. C. Reynolds [92] have re-determined the specific rotatory power of *l*-hyoscyamine in 50 per cent. alcohol, and obtained the value $[\alpha]_D -22°$. The *d*-base gave a slightly lower result, probably owing to racemisation. The rotatory power is not affected by concentration, but the influence of temperature is not mentioned. The paper contains a number of valuable observations on the rotatory powers of different alkaloids and their salts, and also of the influence of different solvents. One of the most striking observations is that hydrastine has a strong dextrorotation in 50 per cent. alcohol, is optically inactive in 95 per cent. alcohol, and lævorotatory in absolute alcohol.

According to F. Klein,[93] when a trace of sodium selenite is added to a solution of an alkaloid in 94 to 95 per cent. sulphuric acid, colorations are produced by means of which several alkaloids may be distinguished.

For the production of the red coloration with adrenaline, potassium persulphate is said to be preferable to other oxidising agents.[94] A solution of vanillin in alcohol containing a little hydro-

[84] *J. Pharm. Chim.*, 1910, [vii], **2**, 20; *A.*, ii, 763.
[85] *Arch. Pharm.*, 1910, **248**, 303.
[86] *Bull. Sci. Pharmacol.*, 1910, **17**, 59; *A.*, ii, 558.
[87] *Arch. Pharm.*, 1910, **248**, 365.
[88] *Ibid.*, 345.
[89] *Schweiz. Wochensch. Chem. und Pharm.*, 1910, **48**, 410.
[90] *Apoth. Zeit.*, 1909, **24**, 662; 1910, **25**, 137; *A.*, ii, 362.
[91] *J. Amer. Chem. Soc.*, 1910, **32**, 132; *A.*, ii, 361.
[92] *Trans.*, 1910, **97**, 1328.
[93] *J. Ind. Eng. Chem.*, 1910, **2**, 389.
[94] A. J. Ewins, *J. Physiol.*, 1910, **40**, 317; *A.*, ii, 557.

chloric acid is said to give a colour reaction with 0·00095 gram of antipyrine, but not with pyramidone.[95]

The assay of anhydromethylenecitric acid, its sodium salt, "citarine," and its compound with hexamethylenetetramine ("helmitol") is dealt with by J. M. A. Hegland.[96]

Fats and Oils.—The comparatively recent introduction of cocoanut oil and of palm kernel oil as materials for the manufacture of margarine renders it important that the methods of detecting and estimating these in presence of other fats should be made as precise as possible. One of the most valuable tests for distinguishing between butter fat and the fats above named is that of Polenske, and in this connexion attention may be drawn to a paper by S. H. Blichfeld.[97] He has devised an apparatus which overcomes the difficulty in the Polenske method of the insoluble acids settling on the condenser tube. He shows that the percentage of the soluble and insoluble silver salts of the volatile fatty acids affords valuable data for the estimation of the above-named fats in admixture with butter. The method proposed by E. Ewers,[98] which is based on the different solubility in water of the magnesium salts of the fatty acids, and on the different solubility in light petroleum of the fatty acids from the soluble magnesium salts, is likely to prove useful, as are also the two methods proposed by G. Fendler.[99] One of these depends on the different solubility of the fatty acids in 60 per cent. alcohol, and the other on the fractional distillation of the ethyl esters of the fatty acids.[1] M. Raffo and G. Foresti [2] describe a viscometric method by means of which they claim that 10 per cent. and upwards of margarine in admixture with butter may be rapidly and accurately estimated. The instrument employed is Ostwald's viscometer. G. Dumitrescu and D. M. Popescu [3] recommend taking the refractive index of the insoluble fatty acids of butter in order to detect sophistication with foreign fats.

A series of investigations has been published on the analysis of wool grease, "oleine." [4] It is shown that cholesterol is either absent or present only in traces, and methods are described for the detection and estimation of mineral and rosin oils in admixture

95 C. Primot, *Bull. Sci. Pharmacol*, 1909, **16**, 270 ; *A.*, ii, 83.

96 *Pharm. Weekblad*, 1910, **47**, 418 ; *A.*, ii, 555.

97 *J. Soc. Chem. Ind.*, 1910, **29**, 792.

98 *Zeitsch. Nahr. Genussm.*, 1910, **19**, 529.

99 *Ibid.*, 545.

1 This paper was, however, published in 1908 (*Arbeiten. Pharm. Inst. Univ. Berlin*, 1908, see *Chem. Zentr.*, 1908, ii, 911).

2 *Gazzetta*, 1909, **39**, ii, 441 ; *A.*, ii, 360.

3 *Ann. Falsif.*, 1910, **3**, 149 ; *A.*, ii, 556.

4 J. Marcusson, *Mitt. K. Materialprüfungsamt.*, 1910, **28**, 469 ; G. Winterfeld and W. Mecklenburg, *ibid.*, 471 ; G. Winterfeld, *ibid.*, 474.

with the above-named "oleine." For the detection of fish oils in vegetable oils, advantage has been taken of the fact that the bromides of the former are insoluble, and of the latter soluble in chloroform.[5]

Halphen's test for cottonseed oil is said to be rendered much more sensitive when the mixture of oil and reagent is heated in a sealed tube at 120°.[6] It has been found that other alcohols may be substituted for amyl alcohol, which is usually employed in this test, but that without any alcohol no coloration appears until the heating has been continued for fifteen minutes, and it is suggested that this may be due to the presence of glycerol produced by hydrolysis. It has also been found that the solution of sulphur in carbon disulphide cannot be replaced by thiocyanates, xanthates, or other sulphur compounds.[7]

For the detection of rape oil or of any oil derived from the *cruciferae* in admixture with other oils, methods depending on the isolation of erucic acid have been proposed.[8] There has been some confusion in the literature between Chinese and Japanese wood oils, both being designated in the trade as Tung oil. A. Kreikenbaum [9] gives some constants of the Chinese product.

It has recently been shown that drying oils give a primary and secondary bromine value, whilst non-drying oils absorb the full amount of bromine at once.[10]

Fermentation Products.—Under the name of "urotropine," hexamethylenetetramine is being added to wines to remove the excess of sulphurous acid in them. It appears merely to mask the sulphurous acid by the formation of the compound with formaldehyde. When a wine so treated is distilled with sulphuric acid, formaldehyde passes over, and may be detected by the ordinary reactions.[11]

The method of estimating tartaric acid in natural products described by C. Beys [12] appears useful and accurate. P. Carles has conducted a useful investigation of the methods for the analysis of

[5] O. Eisenschiml and H. N. Copthorne, *J. Ind. Eng. Chem.*, 1910, **2**, 43.

[6] R. Marcille, *Ann. Falsif.*, 1910, **3**, 235.

[7] L. Rosenthaler, *Zeitsch. Nahr. Genussm.*, 1910, **20**, 453; *A.*, ii, 1123.

[8] D. Holde and J. Marcusson, *Zeitsch. angew. Chem.*, 1910, **23**, 1260; *Chem. Zeit.*, 1910, **34**, 689.

[9] *J. Ind. Eng. Chem.*, 1910, **2**, 205.

[10] W. Vaubel, *Zeitsch. angew. Chem.*, 1910, **23**, 2077; 2078; *A.*, ii, 1122.

[11] Rouillard and Goujon, *Ann. Falsif.*, 1910, **3**, 14; *A.*, ii, 239; G. Denigès, *Compt. rend.*, 1910, **150**, 529; *A.*, ii, 357; A. Hubert, *Ann. Chim. anal.*, 1910, **15**, 100; *A.*, ii, 465; Bonis, *Ann. Falsif.*, 1910, **3**, 106; *A.*, ii, 466; H. Fonzes-Diacon, *Bull. Soc. chim.*, 1910, [iv], **7**, 389; *A.*, ii, 662; E. Voisénet, *Compt. rend.*, 1910, **150**, 879; *A.*, ii, 466; L. Surre, *Ann. Falsif.*, 1910, **3**, 292; *A.*, ii, 808.

[12] *Compt. rend.*, 1910, **150**, 1250; *Bull. Soc. chim.*, 1910, [iv], **7**, 697; *A.*, ii, 662, 758.

tartrates adopted by the Seventh International Congress of Applied Chemistry.[13]

According to G. Meillère and P. Fleury,[14] inositol may be isolated from various fermented liquids, as also from animal fluids and plant juices by precipitation with basic lead acetate, copper acetate, etc. P. Fleury [15] proposes to identify wine vinegars by the presence of inositol. He does not mention, however, whether he has proved the absence of inositol in other fermented vinegars, for example, malt vinegar.

The suggestion has been made by A. Rusconi [16] to detect saponin in beers, aerated waters, and wines by hæmolysis.

A modification of the Allen-Marquardt method of estimating higher alcohols in potable spirits has been described by A. Lasserre,[17] whereby propyl alcohol is excluded. The principle of the method is that the sample is extracted with carbon disulphide in presence of saturated sodium chloride solution, and the extract oxidised.

Turpentine, Petroleum, and other Organic Products.—In the contracts laboratory of the United States Bureau of Chemistry, a large number of commercial materials and products are examined, and the methods which have been found most useful are described by P. H. Walker.[18] The methods which deal with the analysis of paints, pigments, and paint materials, inks, "glycerin," lubricating oils, glue, rubber, disinfectants, pipe covering and cement, and soaps, although in many cases not new, are valuable inasmuch as their accuracy has been so thoroughly tested.

A modification of H. E. Armstrong's well-known method of estimating turpentine and petroleum in mixtures [19] has been described by R. S. Morrell.[20] He obviates the difficulty of separating the petroleum from the polymerised turpentine by distilling the mixture direct with steam, when the petroleum passes over quantitatively. The method is said to be accurate to within 2 per cent. For the estimation of petroleum and resins in turpentine oils, P. Nicolardot and L. Clément [21] add nitric acid to a solution of the sample in glacial acetic acid, and distil. The turpentine is destroyed, petroleum passes over, whilst the residue contains the resins. E. Louise [22] has further developed his method of analysis

[13] *Bull. Soc. chim.*, 1910, [iv], **7**, 586 ; *A.*, ii, 758.

[14] *J. Pharm. Chim.*, 1910, [vii], **1**, 348 ; *A.*, ii, 553.

[15] *Ibid.*, **2**, 264 ; *A.*, ii, 1006.

[16] *Boll. Soc. Med. Chir. Pavia*, 1910 ; *A.*, ii, 559.

[17] *Ann. Chim. anal.*, 1910, **15**, 338 ; *A.*, ii, 1005.

[18] *Bulletin No.* 109, *U.S. Department of Agriculture, Bureau of Chemistry* ; see also *Chem. News*, 1910, **102**, Nos. 2643—2658.

[19] *J. Soc. Chem. Ind.*, 1882, **1**, 478.

[20] *Ibid.*, 1910, **29**, 241.

[21] *Bull. Soc. chim.*, 1910, [iv], **7**, 173 ; *A.*, ii, 460.

[22] *Compt. rend.*, 1910, **150**, 526 ; *A.*, ii, 357.

by miscibility curves, and applied it to the estimation of petroleum and rosin oils in turpentine. Aniline is used to mix with the sample. The method is applicable to the analysis of alcohols, perfumes, etc.[23]

In a series of papers on the digestion of cellulose by domestic animals,[24] it is shown among other things that Simon and Lohrisch's[25] method of estimating cellulose gives low results. A new method of estimating cellulose has been devised by R. Dmochowski and B. Tollens.[26] A. Grégoire and E. Carpiaux[27] describe an apparatus for the estimation of cellulose by Henneberg and Stohmann's method. For the estimation of the degree of tannage of leather, the methods have been revised by J. G. Parker and M. Paul.[28]

Agricultural Chemistry.

L. E. Cavazza[29] proposes to estimate the alkali metals in soil volumetrically as carbonates. The soil is first extracted with hydrochloric acid, and the extract repeatedly evaporated with oxalic acid until all the hydrogen chloride has been expelled. The residue is then ignited, and the soluble portion titrated. Biéler-Chatelan,[30] for the estimation of the available potassium in soils, recommends extracting with water saturated with carbon dioxide.

Densch[31] has reinvestigated his method of estimating nitrogen in soils. For the total nitrogen any nitrite present is first oxidised with permanganate and sulphuric acid. Reduction is next effected by ferrum redactum or zinc dust. The remainder of the operation is the same as in Kjeldahl's method. The author claims that his method so modified is just as accurate as that of Mitscherlich.[32] This last-named method is adversely criticised by T. Zeller.[33]

A scheme for the estimation of different nitrogenous substances present in bone superphosphate is published by G. Chardet.[34]

[23] Compare also M. Vèzes, *Compt. rend.*, 1910, **150**, 698 ; *A.*, ii, 461.

[24] A. Scheunert, E. Lötsch, and W. Grimmer, *Berl. Tierärztl. Wochensch.*, 1909, **25**, 826, 867 ; 1910, **26**, 113, 152 ; *A.*, ii, 554.

[25] *Zeitsch. physiol. Chem.*, 1904, **42**, 55 ; *A.*, 1904, ii, 787.

[26] *J. Landw.*, 1910, **58**, i, 21 ; *A.*, ii, 554, 555.

[27] *Bull. Soc. chim. Belg.*, 1910, **24**, 217 ; *A.*, ii, 661.

[28] *J. Soc. Chem. Ind.*, 1910, **29**, 315.

[29] *Alba. Scuola Vitic. Enol. Jan.*, 1910 ; *A.*, ii, 453.

[30] *Compt. rend.*, 1910, **150**. 716 ; *A.*, ii, 453.

[31] *Chem. Zeit.*, 1909, **33**, 1249 ; *A.*, ii, 70.

[32] *Ann. Report*, 1909 157, 158.

[33] *Landw. Versuchs.-Stat.*, 1909, **71**, 437 ; *A.*, ii, 70.

[34] *Ann. Chim. anal.*, 1910, **15**, 215 ; *A.*, ii, 652.

Water Analysis.

In connexion with the estimation of nitrates by the Grandval and Lajoux method, E. M. Chamot and D. S. Pratt have continued their interesting researches,[35] and they find [36] that the coloration is due *to the formation of tripotassium 6-nitrophenol-2 : 4-disulphonate.* A careful study of the influence of different quantities of chlorides on this method has been made by R. Stewart and J. E. Greaves.[37] It has been pointed out that nitrites in presence of chlorides enhance the coloration given by nitrates in the Grandval and Lajoux method.[38] For the estimation of nitric nitrogen, Salle [39] recommends reduction with zinc dust and ferrous sulphate in presence of sodium hydroxide, and the accuracy of this method has been confirmed by C. Frabot,[40] who finds that reduction by aluminium in alkaline solution is also trustworthy.

A. Vesterberg [41] has applied Winkler's volumetric method of estimating carbon dioxide to a number of cases. With natural waters containing magnesium, the precipitation of magnesium hydroxide is a disturbing factor, but this is said to be overcome partly by adding a certain quantity of sucrose.

It has been shown by M. T. Lecco [42] that for the estimation of lithium in waters, the Meyer-Fresenius method gives results accurate within ± 3 per cent.

Physiological Chemistry.

Amino-compounds.—The very useful Sachsse-Kormann process for the estimation of aliphatic amino-groups was improved by Horace T. Brown and his collaborators some years ago.[43] It has been further modified by D. D. van Slyke,[44] and in the apparatus which he describes an estimation can be made in a few minutes to a degree of accuracy amounting to $\pm 0{\cdot}05$ milligram of nitrogen.

Increasing use is being made of Sörensen's formaldehyde method of estimating amino-nitrogen in physiological liquids, and some most important papers on the subject have appeared during the year.[45]

[35] *Ann. Report*, 1909, 153.

[36] *J. Amer. Chem. Soç.*, 1910, **32**, 630 ; *A.*, ii, 545. [37] *Ibid.*, 756 ; *A.*, ii, 652.

[38] L. Farcy, *Bull. Soc. chim.*, 1909, [iv], **5**, 1090, 1091 ; *A.*, ii, 72 ; I. Pouget, *ibid.*, 1910, [iv], **7**, 449 ; *A.*, ii, 652.

[39] *Ann. Chim. anal.*, 1910, **15**, 103 ; *A.*, ii, 451.

[40] *Ibid.*, 209 ; *A.*, ii, 652.

[41] *Zeitsch. physikal. Chem.*, 1910 ; **70**, 551 ; *A.*, ii, 345.

[42] *Zeitsch. anal. Chem.*, 1910, **49**, 286 ; *A.*, ii, 453.

[43] *Trans., Guinness Research Laboratory*, 1903, **1**, 29. [44] *Ber.*, 1910, **43**, 3171.

[45] V. Henriques and S. P. L. Sörensen, *Zeitsch. physiol. Chem.*, 1909, **63**, 27 ; 1910, **64**, 120 ; *A.*, ii, 164, 466 ; O. von Spindler, *Schweiz. Wochensch. Chem. und*

Attention has been drawn to the necessity of removing carbonates and phosphates previous to titrating a liquid by this method.[46] The fact that many physiological liquids are coloured is a serious difficulty in the application of Sörensen's method, and an apparatus (consisting of glass cells illuminated from below), in which it is stated these titrations can be carried out with sufficient accuracy to justify the ionic concentration being calculated, should prove useful.[47]

Proteins.—Certain proteins of animal origin have been shown to give an intense purple coloration with sodium nitroprusside and ammonia which is discharged with acetic acid, and since this reaction is not given by egg albumin until it has been submitted to peptic digestion, it is surmised that it is due to hydrolysed products of the proteins—organ-peptides.[48] Acetone has been suggested as a precipitant for proteins in milk and blood.[49] For the estimation of albumin in urine, a method consisting in precipitating with picric acid, centrifuging, and measuring the depth of the precipitate is rapid, and probably accurate enough for the purpose.[50]

An adiabatic calorimeter for use with the Berthelot bomb in connexion with the determination of the potential energy of food, fæces, and urine has been devised by F. G. Benedict and H. L. Higgins.[51]

Enzymes.—A remarkable number of papers dealing with enzymes has been published during the year, but only those which apply to analytical chemistry—perhaps by no means the best—can be noticed here. The writer had occasion to point out, in the last report, that Harrison and Gair's method of estimating the diastatic power of malt extracts yields inaccurate results. Recently he has published experiments justifying this criticism.[52] He shows that even the more recent modification of the method suggested by Harrison,[53] although it yields better results, is not always quite accurate, since Kjeldahl's law of proportionality is disregarded.

Pharm., 1909, **47**, 767; *A.*, 1910, ii, 449; H. B. Andresen and M. Lauritzen, *Zeitsch. physiol. Chem.*, 1910, **64**, 21; *A.*, ii, 450.

[46] S. P. L. Sörensen, *Biochem. Zeitsch.*, 1910, **25**, 1; *A.*, ii, 556; H. Malfatti *Zeitsch. physiol. Chem.*, 1910, **66**, 152; *A.*, ii, 662; L. de Jager, *ibid.*, **67**, 1; *A.*, ii, 751.

[47] G. S. Walpole, *Proc. physiol. Soc.*, 1910; *Biochem. J.*, 1910, **5**, 207; *A.*, ii, 541, 995.

[48] W. Arnold, *Bull. Acad. Sci. Cracow*, 1910, A, 56, 61; *A.*, ii, 560.

[49] T. Weyl, *Ber.*, 1910, **43**, 508; *Zeitsch. physiol. Chem.*, 1910, **65**, 246; *A.*, i, 287, ii, 486.

[50] Aufrecht, *Deut. Med. Wochensch.*, 1909, **35**, 2018; *Pharm. Zeit.*, 1910, **65**, 345; *A.*, ii, 560, 663.

[51] *J. Amer. Chem. Soc.*, 1910, **32**, 461; *A.*, ii, 391.

[52] *Chemist and Druggist*, 1910, **76**, 924.

[53] See *Ann. Report*, 1909, 160.

Further, he takes exception to Harrison's practice of returning results to four figures, which the accuracy of the copper reduction method does not justify.[54] H. C. Sherman, E. C. Kendall, and E. D. Clark[55] find that the diastatic power of "taka diastase" may be determined by ascertaining the mass which, in thirty minutes, acting on standard starch paste at 40°, causes the complete disappearance of the iodine reaction. They show that the results run parallel with those obtained by the cupric reduction method when the conversion is kept within the limits of Kjeldahl's law. This is of great theoretical interest, as showing that the hydrolysis of starch by the particular enzyme measured by the disappearance of the iodine reaction is a linear function of the time or mass. In order to measure the diastatic power of pancreatin-amylase, both the cupric reduction and iodine methods failed. The latter was found to give satisfactory results when the hydrolysis of the starch was carried out in presence of sodium chloride and disodium phosphate.[56] The inhibiting effects of various reducing sugars towards the hydrolysis of starch by diastase has been studied by A. Wohl and E. Glimm,[57] who have obtained some interesting results. A rapid test for emulsin, depending upon its cyanogenetic function, has been devised by E. F. Armstrong.[58] This method will probably be useful to the analytical chemist when employed as a test for a cyanogenetic glucoside.

J. Wohlgemuth[59] describes a method for the estimation of the activity of fibrin ferment, and of fibrin ferment in body fluids and organs. E. Abderhalden[60] proposes to detect enzymes in tissues by the formation of tyrosine crystals when the tissues are kept for a few hours in solutions of silk peptone.

In order to estimate the activity of trypsin, A. Palladin[61] has suggested dyeing the protein with a substance such as "spirit blue" before acting on it with the trypsin; the tryptic action may be measured by the intensity of the coloration of the solution.

Toxicology and Forensic Analysis.

Some useful directions are given for the purification of reagents employed in toxicological cases by E. Ludwig.[62] He states that he

[54] Compare A. R. Ling and G. C. Jones, *Analyst*, 1908, **33**, 163; *A.*, 1908, ii, 541.
[55] *J. Amer. Chem. Soc.*, 1910, **32**, 1073; *A.*, ii, 1012.
[56] Compare E. C. Kendall and H. C. Sherman, *ibid.*, 1087; *A.*, i, 799.
[57] *Biochem. Zeitsch.*, 1910, **27**, 349; *A.*, i, 799.
[58] *Proc. physiol. Soc.*, 1910, **33**; *A.*, ii, 668.
[59] *Biochem. Zeitsch.*, 1910, **25**, 79; *A.*, ii, 664.
[60] *Zeitsch. physiol. Chem.*, 1910, **66**, 137; *A.*, ii, 666.
[61] *Pflüger's Archiv*, 1910, **134**, 337; *A.*, ii, 912.
[62] *Pharm. Post*, 1910, **43**, 233.

has detected and estimated phosphorus in exhumed corpses six weeks after burial. In one case he found considerable amounts of hydrogen cyanide four months after death, and in an exhumed corpse nine months after burial atropine could be distinctly recognised. In view of the tendency of formaldehyde to react with different compounds, its use for preserving fragments of organs, etc., would require great caution. It is shown by G. Venturoli and E. Ciacci [63] that it prevents the recognition of cyanides, but not of phosphorus or chloroform. In the case of most alkaloids, it exerts no influence, although morphine is mentioned as one which probably condenses with it.

The suggestion to volatilise mercury as metal by heating a substance containing it with sodium formate in a current of hydrogen [64] appears worthy of attention.

M. T. Lecco [65] states that in the examination of animal organs for volatile poisons, such as phosphorus, the distillate, when oxidised with nitric acid, sometimes yields crystals of oxalic acid, which he finds to be derived from alcohol.

A very large number of papers have appeared during the year on the detection and estimation of cyanides, and some of these are of more than usual importance. After Nietzki and Petri had shown [66] that the *iso*purpuric acid of Hlasiwetz is dicyanopicramic acid, it was obvious that the reaction of a cyanide with picric acid is attended by the reduction of the latter, yet this was not generally recognised. It has, however, been shown by A. C. Chapman [67] that under the conditions of the tests for hydrogen cyanide by means of picric acid, the well-known coloration is due to reduction only. It is therefore not specific, and as a quantitative method must be regarded as empirical. This fact detracts considerably from the value of the method of estimating hydrogen cyanide in blood and tissues which has been proposed by A. D. Waller.[68] J. Moir points out [69] that in presence of copper acetate and acetic acid, the leuco-compound, hydrocœrulignone (tetramethoxydiphenol), is oxidised and coloured red by a trace of hydrogen cyanide. Other tetra-substituted diphenols, as well as benzidine, are said to give colour reactions under the same conditions.

E. Berl and M. Delpy [70] describe a method of estimating hydrogen

[63] *Boll. Chim. Farm.*, 1910, **49**, 129.
[64] A. C. Vournasos, *Compt. rend.*, 1910, **150**, 922 ; *A.*, ii, 549.
[65] *Zeitsch. anal. Chem.*, 1910, **49**, 285 ; *A.*, ii, 461.
[66] *Ber.*, 1900, **33**, 1788 ; *A.*, i, 485.
[67] *Analyst*, 1910, **35**, 469 ; *A.*, ii, 1119.
[68] *Proc. physiol. Soc.*, 1910, xlvii—xlix ; *A.*, ii, 759.
[69] *Proc.*, 1910, **26**, 115.
[70] *Ber.*, 1910, **43**, 1430 ; *A.*, ii, 661.

cyanide tintometrically as Prussian blue, whilst G. Lockemann [71] gives directions for the detection of cyanides in coloured solution by this reaction, and also by converting them into thiocyanates.

The fact that the alkaloids can be precipitated by different nitrophenols is discussed by L. Rosenthaler and P. Görner.[72] G. Jörgensen [73] deals with the detection of morphine in animal organs and excreta.

In connexion with the guaiacum test for blood, it has been pointed out that the delicacy is much increased if alcohol be used as well as turpentine, and still further if the turpentine be replaced by sodium peroxide or sodium perborate.[74] It has been suggested to substitute the benzidine test for the guaiacum in testing for blood.[75] The statement of J. McWeeney,[76] that this test as carried out by Adler is a valuable one for the detection of blood stains, has been denied by F. Bordas,[77] who points out that the reaction is obtained with many other colloids of animal and vegetable origin. He finds, however, that the method is applicable if the catalytic activity of the blood be restored by contact with pure cellulose (filter paper free from iron) even after the blood has been heated to 110°. Several papers have appeared on the hæmochromogen test for blood.[78]

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[71] *Ber.*, 1910, **43**, 2127 ; *A.*, ii, 807.

[72] *Zeitsch. anal. Chem.*, 1910, **49**, 340 ; *A.*, ii, 557.

[73] *Ibid.*, 484 ; *A.*, ii, 763.

[74] B. Bardach and S. Silberstein, *Zeitsch. physiol. Chem.*, 1910, **65**, 511 ; *Chem. Zeit.*, 1910, **34**, 814 ; *A.*, ii, 664, 911 ; see also J. Kratter, *Viertelsjahrschr. ger. Med. öffentl. Sanitätswesen*, 1910, **39**, 42 ; *A.*, ii, 664.

[75] E. Walter, *Deutsch. Med. Wochensch.*, 1910, No. 7 ; *A.*, ii, 665.

[76] *Sci. Proc. Roy. Dublin Soc.*, 1909, **12**, 216 ; *A.*, 1910, ii, 84.

[77] *Compt. rend.*, 1910, **150**, 562 ; *A.*, ii, 364.

[78] Kalmus, *Viertelsjahrschr. ger. Med. öffentl. Sanitätswesen*, 1910, **39**, 57 ; *A.*, ii, 664 ; Mita, *ibid.*, **64** ; *A.*, ii, 665 ; Lochte, *ibid.*, 66 ; *A.*, ii, 665.

PHYSIOLOGICAL CHEMISTRY.

THE year 1910 which has just closed has not seen much change in the personnel of the physiological world. Two eminent men, however, have passed away, and the world is poorer by their absence. One of these is Pflüger, the celebrated head of the Bonn Laboratory. He was a prolific worker and a great fighter; no more shall we have to record either his contributions to the science to which he devoted his life, or the polemical papers which issued from his versatile pen. His name will live in the celebrated Journal which he founded, and which is now edited by his successor in the Bonn chair, Professor Max Verworn. The other loss we have to deplore is that of Dr. Sydney Ringer, whose important contributions to physiological science in the midst of a busy life of medical practice are now universally appreciated. Hardly a paper nowadays appears in which Ringer's solution does not find a mention.

The names of new workers and writers will be found in our pages but it is somewhat sad to find that the number of the younger generation devoting themselves to physiology and its branches is not so great as one would wish. The difficulty of finding demonstrators in this subject, at any rate in this country, is one indication of this fact. This is in part, but only in part, explicable by the foundation of the Beit Scholarships, which have snapped up some of the most promising of the younger men and women. The principal cause is the belated discovery that physiology does not pay. With the exception of a few, a very few, professorships, the stipends considered sufficient by Universities and similar institutions for the members of their scientific staff are so parsimonious that it is no wonder that even those who have special aptitude for scientific work cannot afford to relinquish more lucrative means of obtaining a livelihood.

During the summer, the triennial meeting of the International Congress of Physiology met at Vienna. It was a well-arranged and enjoyable reunion. As is usual in such meetings, the number of papers read was so great, that it proved a little difficult to see the wood because of the trees. Here, as in other recent physiological congresses, the subject of biochemistry overshadowed the other subdivisions of physiology.

The only new book which it is necessary to mention is a Handbook of Comparative Physiology, which is being issued in parts under the editorship of Professor Hans Winterstein. It is a very ambitious undertaking, and first-class collaborators have been pressed into service to write the various articles. It is well known how much physiology is indebted to the frog for the extension of our knowledge; frog's muscles and the frog's heart still remain the object of attack in the investigation of many phenomena. Thus, Langley [1] has this year published papers in relation to his theory of receptive substances, in which frog's muscles have served for his investigations on the action of nicotine and curare. Waller and Veley,[2] also, have been using the same muscles for their work on various drugs, and many papers on the digitalis group of substances have called the frog's heart into requisition.[3] There is, however, no need to multiply instances. During the year, also, papers on bees, fireflies, starfishes, and sea urchins will be found in our index. It is, in fact, becoming increasingly recognised how important comparative and even invertebrate physiology now is; great light is shed by such work on vital problems as a whole, and even in many cases the facts so discovered may be applied to the highest animals, man included. The majority of physiologists, it is true, devote themselves more immediately to the consideration of the human subject, or of animals most nearly related to man. This is because the students they have to teach are mainly medical students, and they are thus rightly forced to regard their subject as the Institutes of Medicine, to use the old name by which physiology was once labelled. Speaking for myself, this is the view of physiology in which I am most interested, as will be shown by subsequent portions of this report, in which I propose to consider at some length certain pathological questions. It therefore came to one in the nature of a surprise, in looking through Winterstein's handbook, to see how voluminous is the work already accomplished in invertebrate fields; for example, in the article on nutrition and alimentation which Biedermann has contributed, there are some hundreds of bibliographical references in the section relating to the nutrition of insects alone.

Turning now to periodical literature, one finds no abatement in the monthly output of papers. If anything, there has been an

[1] *Proc. physiol. Soc.*, 1910, lix, *J. Physiol.*, **40**; *A.*, ii, 797.

[2] *Proc. physiol. Soc.*, 1909, xix, *J. Physiol.*, **39**; *A.*, ii, 55. *Proc. Roy. Soc.*, 1910, B, **82**, 147; *A.*, ii, 228; B, **82**, 205; *A.*, ii, 331; B, **82**, 353; *A.*, ii, 524; B, **82**, 568; *A.*, ii, 986.

[3] See, for instance, Magnus and Miss Sowton, *Arch. expt. Path. Pharm.*, 1910, **63**, 255; *A.*, ii, 986; Kasztan, *ibid.*, 405; *A.*, ii, 1094; Werschinin, *ibid.*, 386; *A.*, ii, 1094; W. Straub, *Biochem. Zeitsch.*, 1910, **28**, 392; *A.*, ii, 1094.

increase, if one may judge by the number of abstracts which have to be prepared. In many cases the papers in the physiological or biochemical journals deal almost exclusively with the pure chemistry of substances occurring in living organisms, and have comparatively little bearing at present on biological questions. In other cases, the researches are continuations of work previously undertaken, or the working out of details in what were before unfinished investigations. Under this head we may place the greater part of Abderhalden's work, in which new analyses of the various kinds of silk, and other proteins, or the detection of peptolytic enzymes in the tissues by his optical method amplify previous researches. In the same way, E. S. London and his colleagues have published numerous additions to their prolonged series of papers on the phenomena of and the laws regulating digestion and absorption. London and Abderhalden run each other very close in the volume of their output. The chemistry of colloids is another fruitful and favourite line of research. Fränkel, Thierfelder, Rosenheim and Tebb, and others are still working and publishing papers on the chemistry of that interesting group of substances known as the lipoids; this subject formed the basis of a very keen debate at the Vienna Congress, the main difference of opinion being the relative importance of these substances in biological processes. Another spirited discussion also occurred on the same afternoon as to whether choline produces a rise or a fall of blood pressure. Modrakowski still maintains, in opposition to all other workers, that it is a pressor substance.[4] The old question as to whether pepsin and rennin are distinct enzymes or not still continues in an unsettled state.[5] Nuclein and purine metabolism is recognised now as one of the most important of the questions confronting physiologists, and Schittenhelm, Bang, W. Jones, Mendel, Mareš, and others are still applying themselves to it.[6] Another interesting series of papers relates to the formation

[4] See for instance, Abderhalden and F. Müller, *Zeitsch. physiol. Chem.*, 1910, **65**, 420; *A.*, ii, 530; *Med. Klinik*, 1910, No. 22; *A.*, ii, 725; F. Müller, *Pflüger's Archiv*, 1910, **134**, 289; *A.*, ii, 881; Mendel and Underhill, *Zentr. Physiol.*, 1910, **24**, 251; *A.*, ii, 735.

[5] See, for instance, W. Sawitsch, *Zeitsch. physiol. Chem.*, 1910, **68**, 12; *A.*, ii, 876; Funk and Niemann, *ibid.*, 263; *A.*, i, 801; Rakoczy, *ibid.*, 421; *A.*, i, 801.

[6] Some of the most important of these papers are the following: Schittenhelm and others, *Zeitsch. physiol. Chem.*, 1909, **63**, 248; *A.*, ii, 52; Wells, *J. Biol. Chem.*, 1910, **7**, 171; *A.*, ii, 322; Schittenhelm and Seisser, *Zeitsch. expt. Path. Ther.*, 1909, **7**, 116 *A.*, ii, 423; F. Sauerland, *Zeitsch. physiol. Chem.*, 1910, **64**, 16; *A.*, i, 345; W. Jones, *ibid.*, **65**, 383; *A.*, ii, 526; Scaffidi, *Biochem. Zeitsch.*, 1910, **25**, 296; *A.*, ii, 626; Schittenhelm, *Zeitsch. physiol. Chem.*, 1910, **66**, 53; *A.*, ii, 625; Wiechowski, *Biochem. Zeitsch.*, 1910, **25**, 431; *A.*, ii, 634; Masing, *Zeitsch. physiol. Chem.*, 1910, **66**, 262; *A.*, ii, 631; Vögtlin and Jones, *ibid.*, 250;

of the acetone group of substances, of which perhaps the most important is that by Dakin, in which he shows that not only is the liver capable, by means of an enzyme, of transforming aceto-acetic acid into β-hydroxybutyric acid, but is also able, by means of another enzyme, of accomplishing the reverse change.[7]

More papers on the metabolism of creatine and creatinine were inevitable after the new views on the subject put forward by Mellanby and others made their appearance; but the points in dispute do not seem nearer settlement, except that all observers are pretty well agreed that the liver is the main seat of the change; another burden is thus added to the duties of this uncomplaining organ, and the new duties have been accumulating with great rapidity during recent years. Blood coagulation has not yielded the usual quota of papers this year, the only one of importance being by Howell,[8] who confirms the view already expressed by Rettger, working in his laboratory, that thrombin is not an enzyme. Amongst the other familiar titles I will allude to one more only, namely, the composition of the Bence-Jones protein. Both Rosenbloom[9] and Williams[10] have brought forward some striking evidence in favour of an entirely new view of its nature; hitherto it has been looked upon as a rather unusual form of proteose; there now seems good ground for the belief that it is related to the mucoid found in osseous tissues; if this is so, the relation between bone disease and its appearance in the urine is intelligible.

I have thus passed in rapid review a few of the most important groups of researches that have been published, and I do not propose to treat any of these at greater length; many of them have been the subject of fuller description in former volumes of these reports. The topics I intend to select for more extended notice this year are, first, the physiology of respiration, which has had new light thrown upon it during the year by some very important investigations; and secondly, a series of pathological problems, such as the Wassermann reaction, anaphylaxis, the chemistry of cancer, sleeping sickness, and possibly one or two others.

A., ii, 631; Bang, *Biochem. Zeitsch.*, 1910, **26**, 293; *A.*, i, 647; Hirokawa, *ibid.*, 441; *A.*, ii, 787; Steudel and Brigl, *Zeitsch. physiol. Chem.*, 1910, **68**, 40; *A.*, i, 703; Ackroyd, *Bio.-Chem. J.*, 1910, **5**, 217; *A.*, ii, 977; Mendel and Lyman, *J. Biol. Chem.*, 1910, **8**, 115; *A.*, ii, 973; F. Mareš, *Pflüger's Archiv*, 1910, **134**, 59; *A.*, ii, 973.

[7] *J. Amer. Med. Assoc.*, 1910, **54**, 1441; *A.*, ii, 632; *J. Biol. Chem.*, 1910, **8**, 97, 105; *A.*, ii, 976, 977.

[8] *Amer. J. Physiol.*, 1910, **26**, 453; *A.*, i, 793.

[9] *Proc. Amer. Soc. Biol. Chemists*, 1909; *J. Biol. Chem.*, 1910, **7**, xiv; *A.*, ii, 731.

[10] *Bio-Chem. J.*, 1910, **5**, 225; *A.*, ii, 981. Another view on the Bence-Jones protein s advanced by Christiaens and others (*J. Pharm. Chim.*, 1910, [vii], **1**, 582; *A.*, ii, 733) that the reaction is not specific, but is given by several members of the protein group.

Respiration.

It is almost a truism to assert that the progress of knowledge mainly depends on the invention of new experimental methods, or the perfection of old ones. Science owes a great deal to the reasoning power of the thinker, and to the acumen of the guesser, but both are alike futile until facts are accurately determined. The improvements of the microscope and of microscopic technique lie at the basis of our present knowledge of structure; the perfection of the calorimeter has enabled workers to state with certainty that the law of the conservation of energy applies to the living organism; the various instruments which enable one to analyse gases both in the air and in the blood have done much to lay the foundations of our knowledge of the respiratory process. There was, however, one instrument which has always been regarded with suspicion, and that was the aerotonometer in its various forms. The object of this instrument is the determination of the tension of the blood-gases; and it was just this doubtfulness in the accuracy of its readings that allowed theorisers a chance of advocating rival views on the mechanism of the gaseous exchange which occurs in the lungs, and is usually spoken of as external respiration. Physiologists were thus divided into two camps; one party consisted of those who followed Pflüger in believing that oxygen entered and carbon dioxide left the blood in obedience to the physical laws of diffusion; and the other party, led by Bohr, of Copenhagen, and Haldane, in this country, maintained what is usually called the vitalistic or secretory view. These observers believed that the cells which line the pulmonary air sacs have the power of piling oxygen into the blood from the alveolar air until its tension in the blood was higher than it is in the air, and in the same way thought that the same cells had the corresponding power of secreting the carbon dioxide in the opposite direction. Text-books on physiology use many pages in discussing the pros and cons of the two theories, and finish by leaving the unfortunate learner in a chaotic state of mind. In the future, such a discussion will be no longer necessary; the question has been finally settled, and this mainly by the invention of a new and accurate aerotonometer. The inventor is August Krogh, and he and his wife have published their work in a most interesting and illuminating series of papers.[11] Their work vindicates and proves up to the hilt the mechanical theory, and is all the more striking as they started their investigations with a bias in favour of the vitalistic view, and issued their papers from Bohr's laboratory, its birthplace.

[11] *Skand. Arch. Physiol.*, 1910, **23**, 179, 193, 200, 217, 224, 236, 248; *A.*, ii, 512.

Haldane's later experiments in reference to carbon dioxide had led him implicitly to abandon the secretory theory in relation to that gas, for the immediate effect on the respiratory centre of changes in the alveolar tension of carbon dioxide could not be explained except on a physical hypothesis. It is satisfactory to be able to chronicle that since Krogh's work has been published, he has admitted the validity of Krogh's criticisms on his method, and he finds on repeating his experiments that diffusion alone will also explain the entrance of oxygen into the blood.[12] He, however, still has a lingering belief that the secretory process is necessary as a supplementary process under certain abnormal conditions.

The aerotonometer, which has made possible this satisfactory state of things, is quite a simple one. In the instruments previously used, the blood was brought into contact with a considerable volume of the gas. In Krogh's apparatus, the volume of the gas is small, consisting only of a bubble, and this is completely surrounded with the blood; it can then be withdrawn into a capillary tube, and measurements of the increase or decrease of its size made with accuracy.

In view of the fact that I have already given full abstracts of Krogh's work, it will be unnecessary again to recapitulate all the steps in his methods and arguments. Those interested in the subject should not neglect to read them in the original. I shall therefore be content with noting how small is the tension difference which is necessary to determine the passage of the gases across the intervening membrane. The thinness of its cells is highly favourable to diffusion of gases, and they are not adapted for secretory work; in this they contrast very forcibly with the cells found lining organs, such as the swim-bladder of fishes, where secretion of oxygen does occur. Indeed, in birds the alveolar epithelium is absent, and the endothelial cells of the capillaries alone have to be traversed by the gases.

External respiration, interesting though it is, is, after all, only a means to an end; that end is the utilisation of oxygen in the tissues; the using up of oxygen in the tissues, and the production there of carbon dioxide constitutes what we call tissue or internal respiration. The oxygen is transported in one direction, and the waste carbon dioxide in the opposite direction by the flowing blood. One gram of hæmoglobin combines with a definite amount of oxygen (1·34 c.c.), and is practically saturated at the atmospheric pressure of oxygen (one-fifth of 760 mm.); if placed in an air pump, the oxyhæmoglobin parts from its load of oxygen at first very slowly, and even at half the normal pressure the hæmoglobin is still nearly

[12] Haldane and Douglas, *Proc. Roy. Soc.*, 1910, B, **82**, 331; *A.*, ii, 511.

saturated; below this, the loss is somewhat more rapid, and in a vacuum all the oxygen is dissociated. The due supply of oxygen is thus kept up to practical saturation of the hæmoglobin at the alveolar tension of oxygen, which is not much below one-fifth of an atmosphere. In order, however, that the tissues may readily get their oxygen, it is not only necessary that the hæmoglobin should obtain its full supply under the ordinary atmospheric conditions, but there is another *sine qua non*—the hæmoglobin must readily part with its oxygen under the pressure conditions which prevail in the tissues; the oxygen must come off from the hæmoglobin first into the blood plasma, in which fluid the fall of oxygen tension is not nearly so great as in the vacuum of an air-pump. In round figures, 1 c.c. of arterial blood contains 0·2 c.c. of oxygen, and the venous blood half this amount. What are the factors in the blood, which are absent in a pure solution of oxyhæmoglobin, which enable it to give up half of its oxygen in the mere fraction of time, at most one second, that it occupies in travelling along the capillary vessels? There are three main circumstances that play a part in assisting the ready dissociation of oxyhæmoglobin; the first of these is the presence of carbon dioxide, and the importance of this factor was first shown by Bohr[13]; how the carbon dioxide acts is not known, for carbon dioxide does not, like carbon monoxide, possess the power of replacing the oxygen of oxyhæmoglobin; it is an undoubted fact all the same, and can be demonstrated by a very simple experiment; if one takes two closed tubes of defibrinated blood, both exposed to the same tension of oxygen, and to one is added a little carbon dioxide, the presence of the latter renders the blood obviously more venous in tint.

The second factor is the high temperature of the body, and the details of this factor have been worked out by Barcroft and King.[14] In muscular exercise with its accompanying rise of temperature, in fever, and in inflammation, the organism or part of it requires oxygen at a more rapid rate than usual; the rise of body temperature enables the blood to meet this demand.

The third factor is that other acids may take the place of or assist carbonic acid in turning out the oxygen; the only acid which has been specially investigated in this relationship is lactic acid; and its importance came into evidence in recent work on respiration at great altitudes[15]; here not only is the rise of body temperature favourable to respiration, but the acidosis which also occurs is

[13] See also a recent paper by Manchot, *Annalen*, 1909, **370**, 241; *A.*, ii, 137.

[14] *J. Physiol.*, 1909, **39**, 374; *A.*, ii, 50.

[15] Caspari and Lœwy, *Biochem. Zeitsch.*, 1910, **27**, 405; *A.*, ii, 969; see also Barcroft and Orbeli, *J. Physiol.*, 1910, **41**, 355.

another effort of nature to compensate for alterations in atmospheric conditions.

The study of the details of tissue respiration as a measure of activity in different organs has also progressed during the last twelve months, and I propose to conclude this section of my report by referring to a few in which I consider the results are of special interest.

The first of these which I will take is the investigation of the metabolism of the surviving warm-blooded heart by E. Rohde.[16] He confirmed many points in relation to the isolated mammalian heart which had been established by previous investigators, for instance, that of Locke and Rosenheim on its capacity to utilise sugar, and of Barcroft and Dixon on its gaseous metabolism. The special feature of Rohde's apparatus (the demonstration of which greatly interested those who attended the Vienna Congress of Physiologists) is that simultaneously with the study of metabolism, it is possible to measure the work of the heart. The metabolic changes are found to run parallel to the amount of work done. In the presence of sugar, not only is the sugar burnt, but other constituents in the heart itself (reserve material) are burnt also, and this leads to the production of carbon dioxide. When sugar and other nutritive material are not supplied in the perfusing fluid, these reserve materials are alone utilisable; these probably originate from fat and protein, and the hypothesis is put forward that the heart forms a sort of internal secretion, in which glycolysis occurs. This last conclusion must be accepted with reserve; the chief value of the research is that accurate data are available to support the thesis that gaseous metabolism is a measure of physiological work, a conclusion which we shall be using in an argument a few paragraphs ahead.

The second organ I will select for mention is the intestine. Brodie and his colleagues[17] have shown that the work of absorption of saline and protein material is accompanied with an increased gaseous metabolism. The intestine, as is well known, consists mainly of two sorts of tissue, muscular and epithelial or cellular. It has been previously shown that, weight for weight, glandular tissue uses more oxygen and gives out more carbon dioxide than muscular tissue does. Muscle doubtless contributes more to the production of animal heat than glands do, but this is because of its bulk, not because of the intensity of the respiratory process. In the intestine the same rule prevails; the cellular elements concerned in absorption are mainly responsible for the increase in the gaseous exchanges.

[16] *Zeitsch. physiol. Chem.*, 1910, **68**, 181; *A.*, ii, 976.
[17] *J. Physiol.*, 1910, **40**, 135, 173; *A.*, ii, 518.

O. Cohnheim,[18] who has also taken up the same organ as an object of study, has been mainly concerned with the gaseous metabolism of the muscular coat of the intestine and stomach. It is satisfactory to be able to state that, although the methods employed in these two series of researches are different, the figures obtained are in substantial agreement. I may take the figures for the organ at rest, and compare them. The amounts of carbon dioxide in c.c. produced per gram per minute are as follows:

1. In intestinal muscle	0·0071	(Cohnheim).
2. In intestinal mucous membrane..	0·0318	(Brodie).
3. In small intestine as a whole......	0·02	(Brodie).
4. ,, ,, ,, ...	0·023	(deduced from a combination of the two sets of figures).

These figures, roughly speaking, are doubled during digestive work. The importance of a consideration of figures such as these does not depend on their absolute values, although, of course, it is always more satisfactory to have accurate figures than rough valuations; they show that the alimentary tract is a factor to be reckoned with in any considerations of the total metabolism of the body, and support the view taken by Zuntz, a view which has been the subject of much controversy, that the work of the digestive tract in actual digestion and absorption is not a negligible consideration.[19]

A third instance of the value of the gaseous-metabolism method in ascertaining the physiological meaning of important processes in the body we owe to the work of Barcroft and Straub [20] on diuretics. We may assume as true that physiological work cannot occur without increased gaseous metabolism, and, conversely, that an increase of such metabolism is a sure proof of physiological activity, as we have already stated in our discussion on cardiac metabolism. If that is so, then if a diuretic produces an increased flow of urine without any increase of gaseous metabolism, it must have produced this result by mechanical means, and not as a result of increased action of the secretory apparatus of the renal cells; this is actually so in the case of certain diuretics, and so Barcroft and Straub have brought forward a piece of most valuable evidence in the elucidation

[18] Cohnheim and Pletneff (*Zeitsch. physiol. Chem.*, 1910, **69**, 89, 96, 102, 106; *A.*, ii, 1079) have used quite different methods from those employed by Brodie; their apparatus is a small one constructed on the principle of the Atwater-Benedict machine. In this relationship, one should also refer to Thunberg's micro-respirometer, which has done good service; for recent work on gaseous exchanges in frog's muscle with this instrument, see Thunberg, *Skand. Arch. Physiol.*, 1909, **22**, 406, 420; *A.*, ii, 54.

[19] Recent papers in support of Zuntz's view which should be consulted are by O. Müller, *Biochem. Zeitsch.*, 1910, **28**, 427, and K. Dahm, *ibid.*, 456; *A.*, ii, 1083.

[20] *J. Physiol.*, 1910, **41**, 145; *A.*, ii, 1090.

of the vexed problem whether urine formation can ever be purely mechanical.

The diuretics they studied fall into two groups: (1) those which produce urine without alteration in the gaseous exchange of the kidney (Ringer's solution, and sodium chloride in hyper- and hypotonic solutions); (2) those which cause increased gaseous exchange (urea, caffeine, sodium sulphate, phloridzin). In the case of urea and caffeine, there is a definite poisoning action, as shown by subsequent depression of the gaseous exchange. The distinctive features of the urine produced by the second class are attained by a process of secretion on the part of the tubules, and not by a process of reabsorption. After poisoning the cells by corrosive sublimate or by the diuretics of the second class, a flow of urine can still be produced by the first class of diuretics; the urine so produced appears to be isotonic with the blood-serum. The special interest of the research is the action of diuretics of the first class, and these produce urine independently of secretory activity (as judged by the absence of increased metabolism), and so their action must be attributed to mechanical filtration. The proteins of the blood plasma, in virtue of their osmotic pressure, would attract water into the blood; the capillary pressure would drive water into the urine. Suppose, for instance, that the capillary pressure is equal to 27 mm. of mercury, and that the osmotic pressure of the proteins is a little lower, say 25, as it probably is in normal circumstances, then the available pressure for filtration would be 2 mm. If the amount of protein in the blood plasma were reduced to half, the osmotic pressure will be reduced to 12·5, and the available filtering pressure is then 14·5, a sevenfold increase, and diuresis will occur. This argument was justified by testing it as follows. The animal was bled very considerably, and the blood replaced by Ringer's solution, containing blood corpuscles in suspension; the diuresis so produced was very considerable, although the blood-pressure was very low; and this was attended with no increase in the gaseous exchange.

Having now discussed this most important physiological subject, I pass now to the consideration of the pathological topics, as outlined in the introductory portion of this report.

No doubt many chemists, seeing papers with such titles as anaphylaxis or the Wassermann reaction, will put them aside, simply because the terms employed are foreign to them. The subjects really, if they were not concealed by the jargon of the specialist, are of the deepest interest, and I hope to be able to explain in language as free from technicalities as possible, and without entering into full details, the meaning of the work in question.

The Wassermann Reaction.

It is well known that the injection of a toxin into an animal leads to the production of an antitoxin; that the injection of foreign blood corpuscles into the blood stream leads to the development in the blood of the animal which has received the injection of a substance (hæmolysin) which is capable of dissolving the foreign corpuscles; that the injection of a foreign protein leads to the development of a substance in the blood capable of causing a precipitation of that protein. These examples serve to illustrate the general truth which underlies modern work on immunity and allied problems. Immunity due to the development of an antidote in the body appears to be limited almost entirely to poisons of protein-like nature; the tolerance which is exhibited towards such drugs as arsenic, or alkaloids, or comparatively simple materials, such as adrenaline, is probably in quite another category of events. The general term now adopted for toxins, etc., which are capable of inducing the organism to meet the attack by the production of an antidote is that of antigen.

Wassermann founded his celebrated biological test for syphilis upon the theory of antigen and anti-substance, and although he was here possibly wrong, yet the test is now recognised as most trustworthy as an empirical one. The original method is a little more tedious and difficult of application than the modifications of it which have since been proposed, but most authorities are agreed that the original method is more certain in its results. The reaction (omitting details in technique) is performed in the following way. A rabbit is immunised against the blood of the ox, that is to say, several doses of washed ox corpuscles are injected into the rabbit. The serum obtained from the blood of the rabbit has then the power of dissolving the red corpuscles of ox blood. This, according to the Ehrlich doctrine, is owing to the presence in the serum of two substances, one an enzyme-like material called the complement, and the other named the amboceptor, which anchors the complement on to the corpuscles, the object of its attack. The complement is not specific, but is found in the serum of normal animals also; the amboceptor is specific; it is the special key necessary to fit the ox corpuscle. Corpuscles of other animals would cause the development of other special keys, or specific amboceptors. There is still another difference between the complement and the amboceptor, and this property enables the investigator to separate them; the the complement is thermolabile, and is destroyed by heating the serum to 56° for thirty minutes; the amboceptor is thermostable, and is not affected by this treatment. The rabbit's serum so heated

is therefore no longer capable of dissolving ox corpuscles. But if the mixture of heated rabbit's serum and ox corpuscles receives an addition of some normal guinea-pig's serum, this supplies the complement, and the ox corpuscles are dissolved.

The next step is the preparation of an aqueous or alcoholic extract of a syphilitic liver (usually obtained from a fœtus), and the collection of a certain amount of serum or cerebro-spinal fluid from the patient suspected of suffering from syphilis. The suspected serum, the extract of syphilitic liver, and a small amount of guinea-pig's serum are then mixed together, and the mixture suitably diluted with saline solution. A series of tubes containing this mixture are then placed in an incubator at 37° for one hour, and the ox corpuscles previously sensitised by the addition of the heated rabbit's serum are then added. The tubes are returned to the incubator for two hours, and then put on ice overnight. The next morning the amount of hæmolysis is observed. A control experiment using normal human serum or cerebro-spinal fluid should be made at the same time; in the control, hæmolysis will, of course, occur. But if the patient is suffering from syphilis, no hæmolysis will take place, and the blood corpuscles will simply have sunk and formed a deposit at the bottom of the tube. This is because the syphilitic serum or cerebro-spinal fluid has combined with the complement of the guinea-pig serum, and this "fixation of the complement" has prevented hæmolysis.

The abandonment of the antigen–anti-substance theory as an explanation of the reaction has followed upon the discovery that extracts of guinea-pig's heart, human heart, soaps, and lecithin may replace the extract of syphilitic liver in the method.[21] But whatever be the true explanation, the reaction is universally accepted as a most trustworthy aid to diagnosis, although it is perhaps most definite when the extract of syphilitic liver is employed.

Sachs and Rondorie pointed out that the manner of dilution with saline solution makes a difference. If the dilution is performed rapidly, the mixture becomes densely opalescent; this can to a large extent be obviated by performing the dilution drop by drop. The opalescence interferes with the power to fix complement, and these observers explain this as a physical result of the size of the particles in suspension. The main result of these workers has been confirmed by Gatz and Inaba,[22] who find the reaction sharper with mixtures that have been diluted slowly, although they doubt whether the physical explanation is the correct one.

In relation to the chemistry of the Wassermann reaction, but little

[21] See, for instance, Browning and others, *Biochem. Zeitsch.*, 1910, **25**, 85; *A.*, ii, 629.

[22] *Ibid.*, 1910, **28**, 374; *A.*, ii, 1093.

is at present known. Mott[23] finds that a fluid giving the reaction fails to do so after the removal of the proteins; Sachs[24] thinks the substance is a globulin; and Noguchi[25] has come to the conclusion that it is attached to the euglobulin, from which it cannot be separated by solvents. As to how this arises in the cerebro-spinal fluid, several suggestions have been offered, one being that it is a transudation from the blood; if it were so, one would expect to find the reaction given in cerebral syphilis, but as a rule the cerebro-spinal fluid does not give the reaction in this disease, although the blood-serum does. It is now pretty well proved that the cerebro-spinal fluid is secreted by the epithelium which covers the choroid plexus,[26] and so Mott was led to make a comparative examination of this structure in general paralysis and other diseases, and found that although the choroid plexus in general paralysis, as compared with other diseases in patients of the same age, showed more frequently cystic degeneration and denudation of the choroidal epithelium, still he was unable to associate the two facts.[27] Another suggestion has been made that the substance responsible for the Wassermann reaction has its origin in the increased number of lymphocytes in the fluid. Lymphocytosis is frequently present both in cerebral syphilis and general paralysis, but in the former disease it may be present, and yet the Wassermann reaction be negative.

The mention of these two diseases side by side needs a word of explanation to the non-medical reader.

Syphilis is a disease which is most widespread in its effects, and in its later stages is accompanied with growths (gummata) and inflammatory conditions in different organs. Among these organs the brain and the spinal cord must be reckoned, and disease here produces most serious results. Nevertheless, syphilis even at this stage is curable, for instance, by mercurial inunction.

After an attack of syphilis has occurred and is cured, the patient is even then threatened with an even more serious danger. He is liable to certain degenerative diseases of the central nervous system, of which locomotor ataxy (tabes dorsalis) and general paralysis of the

[23] F. W. Mott. Oliver-Sharpey Lectures on the Cerebro-spinal Fluid, Royal College of Physicians, London, *Lancet*, July 2 and 9, 1910. I am greatly indebted to these lectures for much which appears in the present section of this report.

[24] Quoted by Mott.

[25] *Ibid.*

[26] W. E. Dixon and Halliburton have shown that an extract of choroid plexus, or choroid gland as it may be called, causes when intravenously injected an abundant flow of cerebro-spinal fluid (*Proc. physiol. Soc.*, 1910, xxx; *J. Physiol.*, **40**; *A.*, ii, 522).

[27] Dixon and Halliburton found that extracts of the choroid plexuses from cases of general paralysis were equally active in promoting the flow of cerebro-spinal fluid as extracts of those from normal men and animals.

insane are the most frequent. Such a condition it is now usual to speak of as para-syphilis. The greater seriousness of para-syphilis is due to the fact that it is, with our present knowledge, not curable.

It not infrequently happens that the symptoms of syphilis and para-syphilis are very much alike, and here comes in the usefulness of the Wassermann reaction. In both classes of disease, the blood-serum gives the reaction, but the cerebro-spinal fluid only gives it, as a rule, in general paralysis and other para-syphilitic affections. Looked at from the patient's point of view, it is worth his sacrificing a small amount of his blood or cerebro-spinal fluid in order that his medical attendant may determine which type of disease he has to deal with; and if the Wassermann reaction is negative in the cerebro-spinal fluid, he has the satisfaction of knowing that he may expect to be restored to health.

Sleeping Sickness.

Chemists who have cultivated the habit of reading or even of glancing through the literature of sciences outside their own cannot have failed to notice how largely the tropical disease, known as sleeping sickness, or African lethargy, has occupied the attention of medical workers during the past few years. The publications of the Royal Society on the subject are now very numerous. Pharmacological journals devote much space to a consideration of the drugs proposed to cure the disease, and this is reflected month by month in the abstracts of our own *Journal*. Syphilis is obviously an important subject with a far-reaching effect on the well-being of the race, and from the Imperial point of view, diseases apt to attack our fellow-subjects in Africa, India, and other places within or near the tropics cannot fail to interest the patriotic Englishman. The Commissions which have been sent out to investigate sleeping sickness have fully justified their existence, for under the leadership of Bruce they have succeeded in demonstrating what is the cause of this mysterious malady which decimated the inhabitants of previously well-populated and prosperous districts of Africa. The disease is caused by a minute animal parasite called a trypanosome, and is infectious because the parasite is carried from one animal or one person to another by means of certain biting flies of the tsetse fly type. If the flies are exterminated, or precautions taken to avoid their bites, the disease can be prevented, and already great progress had been made in this direction. Just as there are different kinds of bacteria, so also varieties of the trypanosome exist, and these produce different symptoms, or have an especial liking for certain species of animals. The general term of all these diseases is trypanosomiasis. In promoting the beneficent results that have already followed the

discovery of the cause of these maladies, the chemist has played little or no part; that we owe to army surgeons, bacteriologists, and zoologists. The work of the chemist and the pharmacologist has come in at another place. It is small comfort to the patient already infected to know that zoologists are studying the habits of the flies, and so trying to prevent other people from being bitten. He wants to be cured. Atoxyl and similar preparations and compounds of arsenic and antimony have been the substances found most beneficial in this direction, and hardly a month passes but what one will find in our pages summaries of elaborate investigations of the chemical nature of these drugs, of fresh compounds prepared likely to be less toxic, or of experimental work on animals and men in the testing of the preparations. I wish it were possible to record that their efforts had been attended with complete success; the success has been partial, and mainly confined to the cure of trypanosomiasis in animals; but such as it is, it bodes well for the future. The name atoxyl was originally given to the most widely employed drug of this class, on the supposition that it was not poisonous to man, though fatal to the trypanosome. The name has been shown to be a misnomer. One has here again the old difficulty of finding something that will kill the parasite without doing harm to the host in which the parasite dwells. As I have indicated, however, this search is by no means hopeless. I have been led into this passing allusion to the subject of sleeping sickness from a consideration of certain aspects of syphilis, for it is now recognised that the latter disease is due to a spirochæte, an organism not unlike the trypanosome, and already some work has been performed in the treatment of syphilis on the lines of the treatment of trypanosomiasis.[28] It is at present too early to state definitely whether good results have accrued, but those who have employed Ehrlich's new arsenical preparation, diaminodihydroxyarsenobenzene, now familiarly known in current medical literature as "606," are most enthusiastic. A recent paper, for instance, by McIntosh and Fildes,[29] concludes with the following paragraph:

"The importance of '606' as a destroyer of spirochætes cannot be over-estimated, even apart from the beneficial effect upon the patient. In those cases in which spirochætes were demonstrable in very large numbers before inoculation, none were found in less than twenty-four hours later, even after prolonged search. This fact has been already fully established. The importance of the observation lies in the probability that cases of syphilis can be rendered practically non-infective in a day or two. If this be true, Ehrlich will have swept away the scourge of 2000 years, and given

[28] See, for instance, F. Blumenthal, *Biochem. Zeitsch.*, 1910, **28**, 91; *A.*, ii, 982.
[29] *Lancet*, 1910, ii, 1684.

into the hands of any State which will avail itself of it a weapon for the forcible suppression of syphilis."

It is only right to state, however, that this optimistic view is not shared by all, and the medical journals will be found to contain statements in a diametrically opposite strain.

Anaphylaxis.

A recently published lecture on anaphylaxis[30] is followed by a bibliography of the subject, containing 184 references. This was in December, 1908. The list of papers might at the present time be easily doubled, for *Zentralblätter*, which deal with such matters, publish abstracts at the rate of about twenty per month. This is just an indication of the large amount of work centring around this important piece of borderland chemistry. The word anaphylaxis dates from 1905, and was coined by C. Richet; he was studying the actions of two poisons obtained from sea anemones, which he named congestin and thalassin, and he found that if a small dose which caused no symptoms in a dog was followed twenty-two days later by another small dose, the animal became ill and usually died. This increased susceptibility took a few weeks to develop, and lasted a considerable time, and the condition of hypersusceptibility or supersensitiveness was named anaphylaxis (*ana* against, *phylaxis* protection). The word implies something opposed to prophylaxis, but the phenomenon is not always harmful; it may be of distinct advantage to the organism. The publication of Richet's work led others to discover that the sea anemone's poisons are not the only ones which can produce the phenomenon, but that other antigens (proteins, toxins, animal serums, and the like) may cause it also. At first sight, the anaphylactic state appears distinctly harmful, and no doubt it is one of the dangers of serum therapy. When, however, a danger is recognised, it is possible to avoid it; in the early days of serum treatment, when the production of immunity was its only known effect, one can hardly doubt that if a second dose was given during the anaphylactic state, severe illness or even death followed; and there are on record cases of sudden death produced in this way. Now that anaphylaxis is a matter of common knowledge, unfortunate mishaps of this kind ought not to occur.

The phenomenon was really known before Richet gave it its name. For instance, in the case of vaccination, the reaction appears after an incubation of four days. In a second vaccination, this period is shortened, and the increased power of the organism to

[30] By John F. Anderson and M. J. Rosenau. The Harvey Lectures, New York, 1910.

react is protective, and the anaphylaxis is in this case prophylactic and beneficial. The tuberculin and mallein reactions are well-known instances of anaphylaxis; these substances are not toxic to healthy individuals, but the tuberculous patient is anaphylactic to tuberculin, and the horse suffering from glanders to mallein. The hypersusceptibility of some people to pollen (hay fever) is another example.

Anaphylaxis has, however, mainly been studied by the injection of serum and foreign proteins into the guinea-pig, the animal usually selected for the purpose. Luckily, from the point of view of therapeutics, horse serum is a comparatively harmless substance, whether it is derived from a normal animal, or from a horse immunised against diphtheria; but a second injection during the anaphylactic state, even when used in small amounts, will possibly be fatal. The most remarkable fact in this relation is the smallness of the dose necessary to produce the exaggerated sensitiveness. A millionth part of a c.c. of horse serum will sometimes be sufficient to produce the effect on a guinea-pig, and 0·000,000,05 gram of egg-white has been stated to be enough. It also requires very small amounts when given in a second injection to produce poisonous symptoms; 0·1 c.c. injected into the peritoneal cavity may cause death, whilst much smaller amounts injected direct into the circulation or into the brain will be fatal. In the face of such small figures, it seems almost hopeless to attempt a chemical explanation of the phenomenon, or to isolate the poisonous principle. The hypersensitive state may further be transmitted by the female guinea-pig to her progeny.

The experiment in which the animal receives its second dose is a very striking one; death usually is a matter of minutes only; the blood pressure falls enormously, the abdominal viscera are gorged with blood, and hæmorrhages are frequent; the bronchial muscles are acutely contracted. J. Auer [31] sensitised guinea-pigs by the subcutaneous injection of 1 to 2 c.c. of horse serum; the maximum sensitiveness was reached about the ninth week, and this was maintained for at least twenty-three weeks more, the longest interval tested. Noting the prominence of bronchial constriction among the symptoms, atropine was used as an antidote, and was found to be of distinct utility; without atropine the death rate was 75, with it only 28 per cent. The view taken by most observers is that the poison acts in this animal upon the respiratory centre.

Numerous theories have naturally been suggested to explain all these remarkable facts; it is a good general rule that when hypotheses are many, the correct explanation has still to be found. It would be impossible to state them all in this brief summary;

[31] *Amer. J. Physiol.*, 1910, **26**, 439; *A.*, ii, 985.

I propose to take one or two as samples. The first selected is that of Gay and Southard.[32] They consider that there is in the serum a substance provisionally termed anaphylactin, which is not absorbed by the guinea-pig's tissues, is not neutralised, and is excreted with great slowness; it therefore remains as a constant irritant to the cells of the body, so that their reactivity for the other constituents of the foreign serum is increased. If then the cells are suddenly presented with a second dose of the serum, they are overwhelmed in the exercise of their increased assimilating functions to such a degree that local or general death may occur.

As is usual in such theorising, it has been found necessary to invent a series of new words; for example, sensibilisinogène, sensibilisine, and antisensibilisine; these figure in Besredka's theory, but in the present state of uncertainty it is not necessary to explain these more fully.

Rosenau and Anderson's work has shown that anaphylaxis is specific, for guinea-pigs may be sensitised to three substances at the same time (milk, serum, and egg-white), and subsequently react to a second injection of each one of these substances, acting as though it was susceptible to three separate infectious diseases. This discovery indicates that chemical changes rather than morphological alterations are at the basis of the phenomenon, and complicates matters by the assumption that many anaphylactins exist.

Richet, who has followed up his work on the poisons of actiniæ with further experiments on other toxins (for example, one extracted from the mussel), thinks that anaphylaxis is due to the presence of a toxigenic substance not poisonous in itself, but capable of producing poison by reacting with the second injection of the extract or serum. In support of this view, he points out that a mixture of the serum of a sensitised dog and of the mussel extract *in vitro* is more toxic than the extract alone.

Vaughan and Wheeler, in view of the circumstance that anaphylaxis can be produced by proteins in a state of comparative purity, believe that the phenomenon must be due to a toxic fragment of the protein molecule.

It is a little difficult for one like myself, who is only able to view pathological questions through physiological spectacles, to appraise the relative merit of the rival theories. It will probably be safer to make no such attempt here, but to be content to await further knowledge. The most recent paper I have read on the subject, however, appears to me to be of great value, and certainly throws a new light upon it. It is written by Dr. W. M. Scott[33]; this investi-

[32] *J. Med. Research*, 1907, **16**, 143; 1908, **18**, 407; 1908, **19**, 1, 5, 17.
[33] *J. Path. Bact.*, 1910, **15**, 31.

gator has performed his experiments on the rabbit, and in this animal the symptoms are not so markedly bronchial as in the guinea-pig; the majority of the symptoms are due to the great fall of blood pressure, and this in its turn is attributed to the active dilatation of the capillaries, which is accompanied by injury to the vitality of the cells of which they are composed. The main interest, however, of the paper occurs in connexion with the answer to the question, What modification has taken place in the economy of the animal to lead to behaviour so vastly different from the normal animal? The fact that the sensitive condition can be transferred to another animal by the serum fixes attention on this fluid as containing the responsible factor. In the serum the precipitin content runs parallel with the severity of the symptoms, and at once suggests that the presence of this and not of any other hypothetical anti-substance (anaphylactin, sensibiline, etc.) is the new factor to which is due the difference between the normal and the sensitive animal. Doerr and Russ [34] have noticed the same correspondence between precipitin strength and lethality in the guinea-pig. The disappearance of the precipitin from the serum after the anaphylactic condition passes off is a point in favour of the same view.

How the interaction of precipitin and antigen acts so as to produce the symptoms and morbid changes is still a matter for speculation. In the now historic phrase, we must be content to "Wait and see."

The Chemistry of Cancer.

Cancer is a subject as important to the well-being of the race as syphilis, and so far as cure of this terrible scourge is concerned, medical men are as far off as ever they were. Those who work under the auspices of the Imperial Cancer Research Fund are a little more hopeful in their reports than they were in previous years, but as Sir Alfred Pearce Gould has recently pointed out, hope is rather of the pious than of the practical kind. I have in previous issues of these Reports stated that in mice a certain fairly large proportion of spontaneous recoveries occur; in man, also, there is a very small percentage of cases which get well without operative interference. Nature therefore has the power to counteract the malady, and it is this circumstance that makes the investigator less hopeless than he was previously. If nature's mode of cure can only be discovered, there is hope for suffering humanity. It is a large "if," but that should not hinder the progress of research.

The reports of the Imperial Cancer Research Fund contain but little that the chemist can get hold of; the bacteriologists and parasitologists have had a long and fruitless innings, and it can

[34] *Zeitsch. Immun. exp. Ther.*, 1910, 4, 706.

hardly be doubted that chemistry will play a part in the ultimate solution of the cancer mystery. This branch of work has not been neglected by those who work outside the enclosure of the Imperial Cancer laboratories, but up to the present little that is definite has been discovered. That there are fundamental changes of a chemical nature in the organism of a cancer patient is undoubted; the limitation or disappearance of the acid of the gastric juice is not a mere local condition of the mucous membrane of the stomach, but an indication of a chemical state widespread throughout the body. It has also been proved beyond question that the blood serum in cases of cancer is very rich in antitrypsin. The mere establishment of this fact has not been without practical importance; a non-malignant tumour will often simulate cancer, and the investigation of the antitryptic power of the serum will do a great deal to settle the question; suppose it is found that there is no rise in the antitryptic value, it is impossible to do more than imagine the relief which will be experienced by the patient; it is like a reprieve to a condemned man on the way to execution. Unfortunately, great hopes were built upon this discovery, which have never been fulfilled. Trypsin was vaunted at one time as a cancer-cure, and the daily Press, encouraged by certain pseudo-scientific men of the same kidney, is greatly to be blamed for thus raising the hope of sufferers. If a few cases of cure can be adduced in support of this treatment, they are probably not more numerous than those of spontaneous recovery just alluded to. Trypsin, after all, is only one of a large group of enzymes; many more remain to be investigated, though at the present stage of the inquiry it would be most unwise to promulgate any theory of a connexion between enzyme-disturbance and the occurrence of malignant disease, and still more unwise to preach that cure lies in the direction of enzyme administration. The rise in the antitryptic value of the serum is also not a specific characteristic of cancer; it is found, also, in other pathological conditions; and in cancer and in these other pathological conditions one is quite in the dark as to whether this sign indicates a factor in the cause of the malady, or is one of its consequences, whether therefore the administration of the enzyme will be favourable or the reverse.

Braunstein and Kepinoff [35] contend that the increased formation of antitrypsin is due to cell degradation and the setting free of intracellular proteolytic or autolytic enzymes. They show that the antitryptic action of the serum can be increased by the injection intraperitoneally of liver or carcinoma paste if the material is not previously heated. If it is heated before injection, no increased antitrypsin formation is observed. In other words, antitrypsin is

[35] *Biochem. Zeitsch.*, 1910, **27**, 170; *A.*, ii, 786.

nature's reply to the injection of an antigen, or to the liberation of antigens by cell degeneration. Such a view has much to commend it, for it is analogous to what so often occurs in other cases. If it is correct, antitrypsin formation is a mere accident in carcinomatous metabolism.

Exactly the same fundamental questions arise in relation to other enzymes, but of these only two series of researches are sufficiently ripe for mention. One of these relates to peptolytic enzymes, the elaboration of the methods for the detection of which belongs to Abderhalden.[36] Various tumours of mice and men were investigated, but the activity of the enzymes present in comparison with those of normal tissues exhibit mainly a difference of degree rather than of kind. One difference of kind was, however, noted, namely, that the juice from malignant tumours produces cleavage of silk peptone, whereas that of normal tissue (liver) does not. Dog's serum normally contains no peptolytic (or erepsin-like) enzymes, so differing from the normal serum of rats and mice; in dogs with malignant tumours, however, some preliminary experiments indicate that peptolytic enzymes are present in their serum.

The second series of investigations relate to the influence of serum on the lipase of pancreatic juice; this has been carried out by Rosenheim and Shaw-Mackenzie.[37] These observers find that serum accelerates the activity of pancreatic lipase; the accelerating substance in the serum dialyses, and is soluble in dilute alcohol; it is inhibited by cholesterol. This power of serum is much less in human than in animal serum, except in certain pathological conditions, of which cancer is one, and the lipoclastic acceleration of the serum runs parallel with its antitryptic power. Since then, Shaw-Mackenzie has found that this lipoclastic acceleration is very high in mice which will not "take" cancer grafts. This is a point in favour of the view that this power is part of the protective mechanism. If so, is it possible to ensure protection by methods which will increase this property of the blood? This is one of the many unanswered questions that a study of cancer raises.

All attempts to find any special toxin in cancerous tumours, any specific protein or nucleoprotein, any peculiarity in the nature or proportion of protein cleavage products[38] have yielded absolutely negative results. The biochemistry of the tumour does not seem to differ from that of normal tissues except in such circumstances as rate of growth, and assimilation of protein material. Cramer and

[36] Abderhalden and others, *Zeitsch. physiol. Chem.*, 1910, **66**, 265, 277; **68**, 312; *A.*, ii, 636, 980.

[37] *Proc. physiol. Soc.*, 1910, viii, xii, xiv; *A.*, ii, 517.

[38] Abderhalden and Medigreceanu, *Zeitsch. physiol. Chem.*, 1910, **69**, 66; *A.*, ii, 1093.

Pringle [39] find that, weight for weight, cancer cells contain only about three-quarters of the protein in ordinary tissue cells, so that a large mass of tumour is built from a comparatively small weight of protein food; the abiuretic products, however, are slightly more abundant in cancer than in normal cells. This, again, is not a characteristic of carcinomatous growths, for fœtal tissues and other rapidly growing tissues have also a relatively low nitrogen percentage.

So far, then, chemists, like the bacteriologists, have in their investigation of cancer drawn mostly blanks. This circumstance, however, has not yet shaken my conviction that in the future the chemist is more likely than anyone else to draw the winning card.

W. D. HALLIBURTON.

[39] *Proc. Roy. Soc.*, 1910, B, **82**, 307, 315; *A.*, ii, 635.

AGRICULTURAL CHEMISTRY AND VEGETABLE PHYSIOLOGY.

DURING the year 1910 no outstanding paper has been published comparable to Russell and Hutchinson's work which appeared during 1909, but activity has been well maintained in all departments of the subject, and particularly in connexion with Vegetable Physiology several valuable and suggestive investigations have been reported. No additions have been made during the year to our knowledge of the action of protozoa in the soil, although several independent investigators have arrived at results which fit in with the theory outlined by Russell and Hutchinson, and in a general discussion on the subject which took place at the Sheffield meeting of the British Association some promising applications to practice were reported in connexion with the treatment of greenhouse soils which, although rich in manure, rapidly become unsuited for vegetation, and again in connexion with the treatment of the soil of sewage farms. In the latter case, it is well known that after the use of excessive quantities of sewage the soil ceases to function in purifying the effluent, and this seems to be connected with such a development of protozoa under the favourable conditions that the bacterial actions are reduced to a minimum, although they may be rapidly restored by submitting the soil to some of the processes of partial sterilisation. One congress of some importance to agricultural science was held during the year, that on "Agro-geology" as a section of the International Geological Congress at Stockholm; there some interesting discussions took place on the classification of soils and on the limits of size to be adopted for the fractions into which a soil is divided by chemical analyses.

Soils.

In previous reports [1] I have discussed various points connected with the theory of soil productiveness and the action of fertilisers which has been advanced by Whitney and his colleagues of the Bureau of Soils in the United States Department of Agriculture,

[1] *Ann. Report*, 1907, 265; 1908, 246; 1909, 191.

but it has always been somewhat difficult to follow the progress of the work. In the first place, it has been printed piecemeal as it arose in the laboratory, and the bulletins are to be found in very few places in Great Britain. Secondly, they are written in a semi-popular style, so that the worker in the same field is rather apt to suspend his judgment until he can see a little more of the experimental foundation and criticise the data. At any rate, from one cause or another, the theory has received but little recognition in Europe, nor have the novel points of view advanced obtained the consideration they deserve. During the year, however, F. K. Cameron,[2] who has been associated with Whitney from the outset, has published a general survey of the whole field, and although the experimental data are necessarily omitted, the reader has now the theory set out in reasonable compass and accessible form, provided with references to the original papers that contain such data as have been given.

The author's main object is to controvert the general idea that the principal function of the soil is to supply nutrients to the plant, and that fertilisers are added to the soil to supply the nutrients which are lacking or in deficient quantity. He begins by discussing the rôle played by the water in the soil in its relation to the solids, and after dealing with the physical actions in which it shares, he takes as a starting point the conclusion that the plant draws its nutriment solely from the solution formed by the action of the soil water on the soil particles. Now Cameron concludes, on physico-chemical grounds, that this solution must be always of approximately the same strength, whatever the soil or whatever the treatment it has received in the way of fertilisers, because the addition of a few pounds of phosphoric acid to a hundred thousand times its weight of soil already containing two or three thousand pounds of phosphoric acid, and with an enormous absorbing power for that material, cannot influence to any sensible degree the concentration of the soil water in the phosphoric acid. Similarly with potash and the other mineral constituents of the plant. The amount of nitrogen in the soil solution is governed by other considerations, and in the main the argument refers to the mineral and not the nitrogenous nutrients of the plant. It is a difficult matter to obtain samples truly representing the soil water, but the evidence points to the extracts from all soils being of approximately uniform composition. Moreover, plants flourish in water cultures of extremely low concentration, far below that prevailing in any of the natural soil solutions, nor is growth accelerated by any increase in their strength.

[2] *J. Physical Chem.*, 1910, **14**, 320, 393; *A.*, ii, 646.

Putting aside the nitrogenous components, it would follow that all soils must behave alike as regards their power of supplying plants with their mineral constituents, and that mineral fertilisers can have no direct action in supplying the plant with its food. As this conclusion does not agree with experience, some other factor must be sought which determines the differences undoubtedly existing between the response of crops on particular soils to mineral fertilisers. The next step in the argument was the examination of aqueous extracts from various soils by the method of water cultures. It was found that plants would grow in these extracts, where they substantially behaved in the same relative fashion as when growing in the soils themselves, either in the field or in pots. The extracts from good soils yielded good plants, while the poor soils transmitted their indifferent crop-producing powers to their aqueous extracts. Nothing in the analyses of these extracts as regards their concentration in plant nutrients would account for the differences in growth exhibited; in fact, dilution of some of the poor extracts resulted in no falling off in growth, but at a certain stage even an increase. Hence the author concludes that the poor extracts and, in their turn, the poor soils contain certain toxic substances which inhibit the growth of plants. This was confirmed by finding that shaking up the poor extracts with such absorbent materials as animal charcoal, precipitated alumina, or ferric oxide made them capable of carrying good growth, although these substances could not possibly have added to the nutrients in the solution. Certain commercial fertilisers had the same beneficial effect on the solution, as had treatment with minute quantities of pyrogallol and lime. From this it was concluded that the toxic substances must be complex organic compounds, which are destroyed or precipitated by the treatment employed. A search was then made in some bad soils for organic materials of a toxic nature, and several such substances were successfully isolated, some of which proved to be toxic to plants in water culture. The author finally correlates the deterioration of soils under the continued growth of one crop with an accumulation of such toxic substances characteristic of a particular plant, and concludes that the value of rotation or a bare fallow or of the ploughing in of a green crop is due to the opportunities afforded for the oxidation or precipitation of the toxins. Furthermore, the usual fertilisers are considered to act indirectly in fitting the soil for the growth of crops rather than in the direct supply of plant food.

I do not propose to repeat here any of the criticisms which have from time to time been offered against some or other of the details of Whitney and Cameron's theory, of which the above is a very

summarised outline. One's general feeling is that nearly every step in the argument is open to some objection either as to fact or interpretation, and one doubtful deduction is based on another until the seeming logic of the whole argument leads to something like topsy-turveydom. Moreover, the final conclusion does not agree with field experience of the action of fertilisers, and it must be remembered that in Europe there is much more minute acquaintance with the effect of particular fertilisers on particular soils and crops than as yet prevails in America with its comparatively extensive methods of farming. It is probably the latter fact that has contributed so largely to the neglect of Whitney and Cameron's theory in Europe, but now that a general statement has been put together in an accessible form, it should receive the consideration of other soil chemists, for whatever their final conclusion about it may be, they cannot fail to find it stimulating and suggestive in a very high degree, suggestive, above all, in driving home the extreme complexity in the processes going on in the soil. It represents the final destruction of what we might call the old Liebig mineral theory, that the one thing needful to fertilise the crop was to put into the soil the substances the crop takes out; incidentally, also, the illusion that one can determine the available as distinct from the total plant food in the soil is again dismissed. This idea was proposed, only to be discarded by Daubeny seventy years ago, but, like so many mistaken points of view, it seems to possess perennial vitality.

Although no absolute distinction can be drawn between available and total plant food in the soil, the opinion continues to grow that information that is of value towards forming an opinion of the fertiliser needs of the soil can be best obtained by a determination of the amount of phosphoric acid and potash soluble in an aqueous solution of carbon dioxide, which is, after all, the chief solvent naturally at work in soils. In this connexion, E. A. Mitscherlich [3] has published a critical study on the solubility in water containing carbon dioxide of the materials present in fertilisers and soils. He ascertained the influence on the resulting concentration of such factors as time, temperature, proportion of carbon dioxide, and the ratio of the amount of solvent to that of material. The results do not, however, permit of summarisation, but should receive the attention of workers in this subject. In another paper the same author [4] investigates the question of whether crop production is influenced at all by the strength of the soil solution in carbon dioxide, which in the laboratory determines its solvent power over minerals. He arranged a series of pot experiments of given soils and manures,

[3] *Landw. Jahrb.*, 1910, **39**, 299. [4] *Ibid.*, 157; *A.*, ii, 236.

watering some with tap water and others with water containing various amounts of carbon dioxide, but obtained no increased yield for the carbon dioxide. He concludes that a small amount of carbon dioxide is sufficiently effective, and that under natural conditions there is always a sufficient production from the roots and from the oxidation of organic matter, hence the application of fertilisers designed specially to increase the amount of carbon dioxide in the soil gases is needless. The use of carbon dioxide saturated water as an analytical agent to deal with soils is also recommended by Biéler-Chatelan.[5]

Arising out of his work with Hutchinson on protozoa, E. J. Russell[6] has investigated the amount of ammonium compounds present as such in soils. Considerable uncertainty attaches to the determinations of ammonia in soils, because in the methods usually adopted the alkali attacks some of the organic nitrogen compounds, and there is a continuous evolution of ammonia as long as the distillation is continued. Russell finds that distillation with alcoholic potash (0·5 to 1·0 per cent.) at reduced pressures (32—35 mm.) shows a sharp end-point at which the evolution of ammonia ceases, and for soils not too rich in organic matter the same end-point is reached by a single distillation with magnesia and water at the same low temperature and pressure. This point Russell considers to represent the conclusion of the evolution of the nitrogen in the soil that was combined as ammonia. Only one or two parts of ammonia per million of soil are found in ordinary soils, rising in very rich garden soils to five or six. This is because the ammonia is kept down to a low limit by its conversion into nitrate by the nitrifying organisms. Thus under field conditions the factor limiting the formation of nitrates is really the preliminary ammonia producing process, and instead of the rate of nitrification it is really the rate of ammonia production that determines the amount of nitrogen available for the crop.

As bearing on the soil materials available for growth, S. U. Pickering[7] has continued his examination of the chemical changes brought about by heating the soil for a short time to various temperatures above and below 100°. He confirms his previous results, that at all temperatures, but especially at 100° and above, there is a considerable formation of soluble organic matter which will serve as plant food, but is toxic in its nature, as shown by its injurious action on the rate of germination of seeds. This injurious material, however, gradually decomposes, probably by oxidation, because the injurious effect disappears when the soil in a moist condition is exposed to the air even under aseptic conditions.

[5] *Compt. rend.*, 1910, **150**, 716; *A.*, ii, 453.
[6] *J. Agric. Sci.*, 1910, **3**, 233; *A.*, ii, 1104. [7] *Ibid.*, 258.

E. J. Russell[8] has also been working at the often debated question of the value of earthworms in cultivated soils. They have generally been regarded as increasing the productiveness of soil by decomposing the organic matter and preparing it for the action of the micro-organisms. Russell shows that previous experimenters have been misled by the nitrogen introduced into the bodies of the earthworms themselves; when this is allowed for, they seem to have no particular effect on the decomposition of organic matter and the production of nitrates. They have, however, considerable effect as cultivators, loosening and mulching the soil, and this may ultimately bring about some action on its fertility, although experimental demonstration would be difficult. Among the papers dealing with soil materials, mention may be made of one by H. Mieth,[9] who tried a series of vegetation experiments in which he employed calcium silicates as sources of calcium. He found that plants easily decompose such precipitated silicates and can take up the calcium from them, so that these compounds may serve as sources of calcium to the plant instead of the carbonate, and this fact the author correlates with the maintenance of neutrality in many soils which show on analysis only a trace of calcium carbonate.

H. E. Annett[10] reports an interesting fact regarding the colour of certain black cotton soils which occupy an area of over 200,000 square miles in India. These soils are not rich in organic matter, and remain black after oxidation with sulphuric acid. The colour proves to be due to a large extent to a black magnetic compound containing 73 per cent. of ferric oxide and 18 per cent. of titanium dioxide.

Soil Bacteriology.

In the domain of soil bacteria, no very novel work is reported. A. Koch[11] has continued his work on the power of *Azotobacter* to accumulate nitrogen in soils to which sugar and other carbohydrates have been added, and has obtained further results in confirmation of those previously reported. He has extended his experiments to small plots of soil, half a metre square, in the open air, and after treatment with sugar he has found that he obtained an increase of crop, which, although slight in the first year, was considerable in the second and third after application. From other sources we have evidence that the fixation of nitrogen by *Azotobacter* in the open ground is much affected by the prevailing temperature; if

[8] *J. Agric. Sci.*, 1910, **3**, 246.
[9] *Landw. Versuchs.-Stat.*, 1910, **74**, 81; *A.*, ii, 1105.
[10] *Mem. Dept. Agric., India*, 1910, **1**, 185; *A.*, ii, 535.
[11] *J. Landw.*, 1909, **57**, 269; *A.*, ii, 60.

this be too low, other organisms than the *Azotobacter* predominate as a result of the carbohydrate application. Koch has added one further link to the completeness of the demonstration by showing that the addition of sugar to soils destitute of the *Azotobacter* organisms results in no increase in their content of nitrogen.

Koch [12] has also studied afresh the denitrification process in soils, and finds that there is but little loss of nitrogen, although both nitrate and dextrose had been added, provided the amount of water in the soil is kept down. For example, when the water in a particular soil was below 18 per cent., there was no reduction of nitrate, but when it rose to 25 or 30 per cent., denitrification set in. In other words, anærobic conditions must be established before the reducing organism comes into play.

Chemistry of the Growing Plant.

One of the most suggestive papers of the year is that published by H. E. and E. F. Armstrong [13] on the action of chloroform and similar substances in stimulating enzyme action in living structures.

Starting with the interesting observations of Guignard and of Mirande,[14] on the action of chloroform and similar anæsthetics on the development of hydrocyanic acid from cyanogenetic glucosides in the leaves of laurel and similar plants, the Armstrongs have proceeded to generalise the phenomena there described. They make use of the method discovered by Guignard, in which the green leaf is placed in a test-tube with a strip of paper coloured orange-yellow with a solution of sodium picrate. The liberation of a trace of hydrocyanic acid results in the production of successively orange, rose, and finally a dark brick-red colour on the test paper, due to the formation of sodium *iso*purpurate. Using leaves of the cherry-laurel (*Prunus laurocerasus*), which contains the glucoside *prulaurasin*,[15] no hydrocyanic acid is developed when the leaf and test paper are alone in the tube, but the addition of a drop of chloroform is followed in the course of a few minutes by a gradual development of colour, the action being more rapid at higher temperatures.

It was found the solutions could be substituted for the vapour, because sound leaves, partly immersed in water, give no hydrocyanic acid in three or four days. The experiments then showed that the vapours of ammonia, carbon disulphide, chloroform, toluene, ether, and various alcohols were quickly active, benzene, naphthalene, thymol, acetic acid were less so; carbon dioxide, benzene,

[12] *Centr. Bakt. Par.*, 1910, ii, **26**, 335; *A.*, ii, 333.
[13] *Proc. Roy. Soc.*, 1910, **82**, B, 588; *A.*, ii, 883.
[14] *Compt. rend.*, 1909, **149**, 91, 140; *A.*, 1909, ii, 823, 824.
[15] Caldwell and Courtauld, *Trans.*, 1907, **91**, 671.

limonene were only slowly active. In solutions few salts had any action except in strengths that destroyed the leaf, but solutions of sodium or potassium fluorides were active, as were solutions of mercuric chloride and cadmium iodide and of ammonia, but not of potassium or sodium hydroxides.

These results fall into line with the well-known work of A. J. Brown[16] on the semi-permeability of the membrane surrounding the barley grain, and indicate that only those substances are active which succeed in penetrating into the leaf. The authors propose to extend Starling's term of " hormones " to these excitants, and they point out that they are all substances with but slight attraction for water; materials which react with water generally fail to penetrate the leaf.

It is generally considered that in plant tissues the enzymes and glucosides are either contained in different cells or in different vacuoles in the same cell. Guignard states that in the cherry laurel the enzyme is stored in the endodermis, whilst the glucoside is in the parenchyma, and as the enzyme is not diffusible, it is most probable that the glucoside is induced to travel to the enzyme.

The action is evidently bound up with changes in the concentration of the fluids within the leaf; in his paper Guignard compares the action to that of frost, which induces a concentration of the cell sap and at once sets up change. In the leaves exposed to vapours there is sufficient water to allow of the passage of the glucoside towards the " hormone " entering very close to the enzyme which lies near the exterior surface.

From solutions a considerable amount of water enters the leaf with the hormone, a leaf, for example, increases in weight by 20 per cent. after eighteen hours' immersion in chloroform water, whereas it only gains 5 per cent. after twenty-four hours in pure water, and 2 per cent. after forty-five hours in a 2 per cent. solution of sodium chloride.

The authors discuss these results in the light of H. E. Armstrong's theory of the constitution of water, and then proceed to show their application to a number of phenomena in the life of animals and plants. As regards plants, one of the most significant facts is that carbon dioxide itself acts as a hormone; it is easy to suppose that variations in the presentation of this substance to the cell may excite enzymic action in the direction of hydrolysis or the reverse, the most significant of the processes in the metabolism of the cell. Moreover, a slight initial excitation may be sufficient to set in motion considerable change, because many of the products of hydrolysis, for example, hydrocyanic acid and benzaldehyde, are

[16] *Proc. Roy. Soc.*, 1909, **81**, B, 82; *A.*, 1909, ii, 386.

themselves hormones and would extend the action. In the living plant, the hormone-excited changes can never be so large as in the experiments on the detached leaves, for A. D. Waller [17] shows that the leaf is killed within a minute of the action of the chloroform, as may be ascertained from the abolition of electrical response.

Doubtless from these experiments light will eventually be thrown on the physiological function of many of the ethereal oils, terpenes, and scents secreted by plants so normally that they cannot be without significance.

They also throw some light on the horticultural practice which has been worked out of recent years, by which plants like lilacs intended for forcing are exposed to the vapour of ether for twenty-four hours or so. After the etherising process, it is found that the plants can be forced into bloom a week or ten days earlier than would otherwise have been possible. As cold acts in the same way by altering the concentration of the cell sap, we may also correlate the similar acceleration of flowering that is induced by a preliminary cold storage before forcing, and, again, the well-known fact that potatoes which have been frozen become sweet through an accumulation of enzyme-produced sugar. In a paper on the ripening of premature fruit, A. E. Vinson [18] shows that dates which have reached a certain stage of development can be made to ripen by exposure to certain vapours or solutions, practically the same substances which the Armstrongs have found to be active. Vinson similarly concludes that the ripening is brought about by the release of the intercellular enzymes through substances penetrating the cuticle and stimulating the protoplasm.

The field of work thus opened up is extremely suggestive, and promises not only to throw light on many of the processes of the living plant, but also to find certain immediate practical applications.

Various papers dealing with assimilation have been published during the year. S. B. Schryver [19] has taken up afresh the work of Priestley and Usher on the photochemical formation of formaldehyde by chlorophyll. He finds that grass, when washed with warm water, yields no formaldehyde, but when the grass is extracted with alcohol and the dried extract is heated with ether, then formaldehyde can be detected. Hence he concludes that in living plants the chlorophyll contains formaldehyde in combination. He next obtained films of chlorophyll by evaporating a 1 per cent. solution in ether on glass slips at the ordinary temperature. These

[17] *Proc. Roy. Soc.*, 1910, **82**, B, 574; compare *A.*, ii, 741.
[18] *J. Amer. Chem. Soc.*, 1910, **32**, 208; *A.*, ii, 336.
[19] *Proc. Roy. Soc.*, 1910, **82**, B, 226; *A.*, ii, 334.

were exposed to moist carbon dioxide and to air freed from carbon dioxide by soda-lime, both in sunlight and in the dark. No formaldehyde was detected after exposure in the dark, and very little on the slips which had been kept over soda-lime, but a distinct reaction was obtained in sunlight. Schryver concludes that chlorophyll can form formaldehyde directly, but that it rarely becomes sensible because it does not accumulate in the cell, since it is withdrawn to form sugars as fast as it is formed. He employed a sensitive form of Rimini's test for formaldehyde (phenylhydrazine hydrochloride with potassium ferricyanide and hydrochloric acid gives a brilliant magenta colour in presence of formaldehyde), which will detect one part in a million, and can be made quantitative.

Thoday [20] has examined in detail Sachs' method of measuring assimilation by the difference in dry weight of comparable areas in the two halves of a leaf before and after exposure to light. He has succeeded in improving the method by eliminating certain errors, particularly those due to shrinkage of area, to which the method is liable. He obtains rates of assimilation (17 milligrams per hour per square dcm.) even higher than those of Sachs, and much higher than those obtained by Brown and Escombe. The low figures of the latter workers he considers to have been due to the high temperature prevailing in the glass cases in which their leaves were confined, and to the resulting lack of turgor in the leaves which would result in only a partial opening of the stomata.

R. Willstätter [21] and his colleagues have continued their investigations on the constitution of chlorophyll. They had before established the existence of two chlorophylls, one amorphous—a phytol ester containing one phytol residue and one methoxyl group for each magnesium atom—and the other crystalline, yielding, on hydrolysis, phæophorbin, which is a dimethyl ester. The authors have now examined the distribution of these chlorophylls in a number of plants from the various orders. From experiments with grass, plantain, and nettles, they find that the nature of the chlorophyll is not influenced by the soil or the time of the year. The amorphous phytol ester, chlorophyll, is widely distributed and preponderates in some cases. Crystalline chlorophyll is not always found. Colorimetric determinations show that the leaves of various plants contain half to one per cent. of chlorophyll in their dry material.

The question of the action of small traces of metallic salts and other possible catalytic agents on the growth of plants has again received a good deal of attention during the year. For example,

[20] *Proc. Roy. Soc.*, 1910, B, **82**, 421 ; *A.*, ii, 800.
[21] Willstätter, F. Hocheder, and E. Hug, *Annalen*, 1910, **371**, 1 ; *A.*, ii, 150.

in the Rothamsted Laboratory, W. E. Brenchley[22] has examined in considerable detail the effect of the sulphates of copper and manganese on the growth of barley in water cultures. It has been maintained that all substances toxic to plants act as stimuli at some stage of high dilution, but with copper sulphate the author can find no evidence of stimulus even down to a dilution of one part in 10 millions of water. The toxic effect was always manifest, although it was greatly reduced when the copper was added to a solution of nutrient salts and not used in water alone. In the latter case, seedlings are very susceptible, being checked and even stopped in growth by the use of water which has been distilled from the ordinary copper vessels in the laboratory. The stimulus effect which had been reported from time to time may have either been due to accidental variations, since the individuality of plants grown in water cultures is very marked and large numbers must be taken in order to obtain smooth results, or else to some secondary action of the toxic substances on bacteria, etc., in the culture medium. Manganese sulphate can hardly be regarded as toxic for barley; although in moderate concentrations (more than one in 10,000) there was retardation of growth, at lower concentrations, one per 100,000 and downwards, there was distinct evidence of stimulus. Incidentally it was noted that at such concentrations as one per 10,000, the manganese taken up by the plant was excreted as peroxide on the surface of the leaves. As manganese is usually found in plant ashes, and has been considered by Bertrand and his co-workers to aid in the action of the oxydases of the leaf, it obviously stands in a different position, and cannot be compared with substances like copper which are toxic and have no normal physiological function.

In the same line of work comes a paper by P. Ehrenberg[23] on the effect of zinc salts on vegetation. Zinc he finds to be always toxic when the action is simply between the plant and the reacting substance. In his experiments on soil, however, cases were met with of apparent stimulus due to zinc, but the author considers that these can always be explained by some indirect chemical or biological action of the zinc on the constituents in the soil, rather than to any stimulating action of the toxin on the plant. Ehrenberg concludes that zinc vessels ought never to be used in vegetation experiments, although one of the most commonly employed types of vessel for pot culture work is made of zinc.

P. Koenig[24] also reports a long series of experiments on the action of chromium salts on vegetation, in which he claims to

[22] *Ann. of Botany*, 1910, **24**, 571; *A.*, ii, 889.
[23] *Landw. Versuchs.-Stat.*, 1910, **73**, 15; *A.*, ii, 236.
[24] *Landw. Jahrb.*, 1910, **39**, 775.

demonstrate that both the chromium salts and the chromates, although normally toxic, may act as stimuli. The conclusion as to stimulus is, however, vitiated by the fact that the additions of chromium were always made to soil in which the test plants were growing. So involved are the actions taking place in the soil, the resultant only of which is represented by the growth of the plant, that one has no right to draw any conclusions from such experiments as to the direct action on the plant of the material under investigation.

Amongst other work dealing with the living plant which possesses some economic interest is a paper by Otto and Kooper[25] on the changes of the composition of fruit as it ripens after gathering. The experiments were made with sloes, and the authors found that in the ripening process the lævulose increased while the dextrose decreased, and during the same time both the acids and the amount of tannin markedly decreased. The decrease in acid and tannin was larger than the net increase of sugar, the difference no doubt representing losses by respiration, and the authors considered that the other figures indicated a change from dextrose to lævulose, a change, however, which is very difficult to credit.

Another paper, although a contribution to the study of genetics, is yet of general interest to plant-physiologists because of its possible bearing on enzyme actions in living plants, is one by M. Wheldale[26] on the inheritance of colour in certain sweet peas and stocks. In these flowers the colours are due to anthocyanins, which are the oxidised products of the action of an oxydase on a chromogen. Both must be present in the same flower to cause colour, but as all the white flowers contain the chromogen, their absence of colour must be due to a lack of one or other of the factors (peroxide and peroxydase) making up the oxydase system. Investigations of white flowers which on mating will yet throw coloured blooms confirmed this theory; in the extracts of some of the white flowers no evidence of oxydase was found, whilst in others the peroxide factor was lacking. The two factors are inherited separately on Mendelian lines, and, on mating, coloured flowers may be produced when the two factors are again united in the same cell.

Manures and Manuring.

During the year little work on fertilisers has been reported beyond the usual stock experiments on the effect of these materials when used with different crops and soils. Various new materials have

[25] *Zeitsch. Nahr. Genussm.*, 1910, **19**, 10; *A.*, ii, 233.

[26] *Roy. Soc. Report to Evolution Committee*, 1909, V, 26; compare *A.*, 1909, ii, 604.

been brought forward, but none of them represent any fresh development or utilisation of a novel principle as did the nitrogenous manures generated from the atmosphere. In the latter connexion, the changes taking place when cyanamide is applied to the soil continue to attract a good deal of attention, and C. Ulpiani [27] gives an account of a long series of experiments on this question. He dismisses the idea originally suggested by Löhnis that bacterial actions play any considerable part in breaking down the cyanamide to the stage of ammonia. He regards the action as chiefly brought about by the colloidal surface of soil particles, which acts as a catalyst. The change ceases when this is destroyed either by heating the soil or by treating with acids or alkalis, but can be restored by the addition of precipitated silica. The cyanamide changes first into carbamide, and then into ammonium carbonate, but Ulpiani can find no evidence for Löhnis' idea that a formation of ammonium cyanate precedes the carbamide. The change takes place in the presence of antiseptics and with sterilised materials; it also goes on with increased velocity at 100°; again it is most rapid at first, and then falls off. It also increases with the concentrations of the solutions taken. None of these facts agrees with the theory that the change is brought about by bacteria. The soil absorbs the ammonia as it is formed, and this removal of the products accelerates the rate of change, and also prevents polymerisation into dicyanodiamide. Because of the susceptibility of cyanamide to change in moist air and the formation of the toxic dicyanodiamide, C. Brioux [28] has worked out a method for the analysis of the altered product. This method depends on the fact that the precipitate which cyanamide gives with silver nitrate is insoluble in ammonia, whereas the precipitate similarly formed by dicyanodiamide is soluble.

Methods for the estimation of nitrates continue to attract a good deal of attention, because the determinations with the nitrometer or as nitric oxide by Schloesing's process are not particularly convenient. It is obviously preferable to reduce the nitrate to ammonia, which can be rapidly and accurately measured by the routine methods of the laboratory. M. E. Pozzi-Escot [29] employed for this purpose aluminium, together with a little mercuric chloride, so as to form an aluminium-mercury couple which reduces the nitrate to ammonia in a few minutes. This method has, however, been severely criticised; Cahen [30] dismisses it as untrustworthy, and would replace it by Devarda's method, in which the reduction is effected by 2 or 3 grams of alloy containing 45 per cent. of

[27] *Gazzetta*, 1910, **40**, i, 613; *A.*, ii, 890.
[28] *Ann. Chim. anal.*, 1910, **15**, 341; *A.*, ii, 1010.
[29] *Bull. Assoc. Chim. Sucr. dist.*, 1909, **27**, 457; *A.*, ii, 71, 153, 652.
[30] *Analyst*, 1910, **35**, 307.

aluminium, 5 of zinc, and 50 of copper. This is digested with the nitrate-containing material for half an hour in the presence of concentrated sodium hydroxide, the digestion flask being connected from the outset by the distilling apparatus. The distillation is then completed and the ammonia collected in the standard acid as usual.

J. M. Wilkie[31] has discussed a method of determining ammonia, which may on occasion become useful to the agricultural analyst. The solution is rendered exactly neutral, and neutral formaldehyde is added. The acid which results from the abstraction of the ammonia by the formaldehyde is titrated with baryta water, using phenolphthalein as indicator.

Chemistry of Animal Nutrition.

Papers dealing with animal nutrition have been rare in this country, but there are not wanting indications that work on this important subject is beginning in Britain, and we are pleased to be able to report on one interesting piece of work that has appeared during the past year. In some earlier papers, T. B. Wood[32] has shown that certain constant differences exist in the composition of the various kinds of mangolds usually grown. Their average content of dry matter varies from 10·7 per cent. in the "Yellow Globe" to 13·1 per cent. in the "Long Red" and yellow-fleshed varieties. Since the "Long Red" yields on the average as large a crop as the "Yellow Globe," and a much larger one than the yellow-fleshed varieties, it produces the most dry matter per acre, and should be the most profitable mangold to grow. To make this conclusion valid, however, it was necessary to show that the dry matter of the "Long Red" variety possesses equal feeding value to that of the others, and accordingly the author carried out a series of seven experiments on fattening cattle, using thirty-seven animals in all, comparing in each case the effect of equal weights of "Long Red" and "Yellow Globe" mangolds. The final result shows a superiority of the "Long Red" as compared to the "Yellow Globe" of 116 to 100 in their power of producing live-weight increase, the proportion of dry matter being as 120 to 100. Two other experiments showed that "Long Red" and yellow-fleshed mangolds possess equal feeding values, the percentages of dry matter being approximately the same in the two varieties. The limits of experimental error obtaining in the trials are discussed, and the final result may be taken as conclusive that the feeding value of the mangold is determined as

[31] *J. Soc. Chem. Ind.*, 1910, **29**, 6; *A.*, ii, 240.
[32] *J. Agric. Sci.*, 1910, **3**, 225.

closely as it can be measured in practice by the percentage of dry matter in the roots.

In the field of animal nutrition interest is now chiefly fixed on the proteins and their cleavage products, as it is felt that the main lines of the energy question are settled. Abderhalden [33] and his co-workers continue to improve upon their attempts to feed animals with the cleavage products instead of the proteins themselves, and have now attained a much greater measure of success. They found that dogs could maintain their nitrogen equilibrium on the deficient cleavage products of meat, whether hydrolysed by pepsin, trypsin, and erepsin, or by acid, provided that care was taken to remove the traces of barium which acted prejudicially in their former experiments. When the products of acid hydrolysis are administered, it is desirable to add tryptophan, because this substance is to a large extent destroyed by the acid.

Osborne [34] has continued his work on the cleavage products of proteins, and in an important paper, in which he sets out as fully as possible the cleavage products of zein, he shows a recovery of something like 80 per cent. He discusses at length the sources of loss which still exist in all methods of protein hydrolysis.

Kellner [35] has continued his work on the value of non-protein nitrogen compounds in the nutrition of ruminant animals. Lambs were fed as to their nitrogenous requirements exclusively on asparagine and ammonium acetate. The result showed that these substances can be so converted by the bacteria of the intestines into protein that they can replace some of the protein required for maintenance. There was, however, no evidence of production of flesh from these non-proteins, but when fed together with protein they can increase the formation of flesh by saving the protein required for maintenance. The same question has also been investigated at the Hohenheim station,[36] where ammonium acetate and asparagine were fed to milch cows. The authors conclude that these substances do not lead to any increase in the undigested protein in the fæces, although they are converted by bacterial action into proteins which may be utilised by the animal, not merely for maintenance, but also for milk production.

Among other papers interesting to the agricultural chemist is one by Siegfeld [37] on the constitution of butter fat. He finds that

[33] *Zeitsch. physiol. Chem.*, 1910, **64**, 158; *A.*, ii, 322.

[34] T. B. Osborne and L. M. Liddle, *Amer. J. Physiol.*, 1910, **26**, 295 *A.*, i, 598.

[35] O. Kellner, P. Eisenkolbe, R. Flebbe, and R. Neumann, *Landw. Versuchs.-Stat.*, 1910, **72**, 437; *A.*, ii, 424.

[36] A. Morgen, C. Berger, and F. Westhausser, *ibid.*, **73**, 285.

[37] *Milchw. Zentr.*, 1910, **6**, 122; *A.*, ii, 327.

tributyrin is soluble in alcohol, by which it can be extracted from a mixture of beef butter. Butter, however, yields very little fat to alcohol, and that of much the same composition as the original fat: from which he concludes that Bell's original conception of butter fat as mixed glycerides is most likely to be correct.

T. Weyl[38] has examined the precipitation of proteins by acetone as a basis for analytical processes. He finds that acetone precipitates the protein from milk completely; the milk is diluted with an equal volume of water, four volumes of acetone are added, and the collected precipitate, after washing, is extracted with ether, dried, and weighed. It is possible that this method of precipitating proteins with but little change may become useful in plant analysis.

As regard the nutrition of farm stock, the most notable event of late years has been the introduction of the soya bean from Manchuria, and the considerable trade in soya bean cake which has thus developed. Although the ordinary analyses show that one was dealing with a very rich material, only paralleled by decorticated cotton cake, direct experiments on its digestibility were not available, but one had to assume that it would probably fall into line with similar concentrated foods and prove very completely digestible.

F. Honcamp[39] now reports certain determinations of the digestibility by sheep of soya bean meal, made both from the pressed cake and from the residue after the oil had been chemically extracted. The following table will show that the meal is the most concentrated of all feeding stuffs in common use, with the exception of linseed from which the oil has not been extracted:

	Press cake.		Residue.	
	Total.	Digestible.	Total.	Digestible.
Crude protein	47·9	43·3	52·2	48·0
Nitrogen-free extract ...	32 8	31·1	34·6	34·6
Crude fat	7·9	6·9	1·8	1·2
Crude fibre	5·6	4·4	5·3	5·2
Starch equiv.	92		86	

It has long been recognised that a certain amount of care must be exercised in feeding stock with cottonseed cake; from time to time injurious results have been reported, as though the feeding stuffs contained some toxic substance, but the experiences were not consistent, and attempts to isolate a poisonous constituent have not been successful, although cholin and betain have been found and credited with the harmful action. In practice farmers have found it wise not to feed cotton cake to milch cows near calving,

38 *Ber.*, 1910, **43**, 508; *A.*, i, 287.
39 *Landw. Versuchs.-Stat.*, 1910, **73**, 241.

nor to young stock. A. C. Crawford,[40] after a series of chemical and physiological experiments, now attributes the toxic results to salts of pyrophosphoric acid, the compounds being in some meals inorganic, in others probably organic. Seed of upland cotton is more generally poisonous than that from Sea Island cotton, although the latter becomes toxic if it is heated in the process of extracting the oil, due to the conversion of ortho- into pyro-phosphates.

Crawford's conclusions seem to be well supported by his experimental work, and it should be noted that at least one previous worker has found pyrophosphates in cottonseed meal and has drawn attention to their poisonous character.

A. D. HALL.

[40] *J. Pharm. Exp. Ther.*, 1910, **1**, 519.

MINERALOGICAL CHEMISTRY.

FROM a purely mineralogical point of view the year 1910 cannot be regarded as particularly eventful. The new minerals we have to record are neither numerous nor specially remarkable, and very little fresh light has been thrown on the more obscure problems of mineralogical chemistry. Large numbers of analyses of minerals have been published, but many of these have been made rather to aid identification than with the express object of arriving at a formula, and it will only be possible to admit to our chronicle analyses made with special care on selected material, or which are of unusual interest on account of the peculiar character or rarity of the species to which they refer. In the borderland where the confines of physical chemistry, mineralogy, and geology meet, a good deal of activity has been manifested, and there is an increasing tendency to attempt to elucidate the complex problems presented by silicate fusions by the study of the behaviour of pure artificial silicates and inorganic salts.

Although interesting results have been arrived at in this field, it is in another direction that progress has been most rapid. The application of the Barlow-Pope theory of crystal structure to the data of organic chemistry has rendered clear much that has hitherto been mysterious and obscure, and has so stimulated the somewhat languishing study of chemical crystallography that it has seemed advisable to include in this report a section in which the more remarkable of the advances made may be briefly indicated. So much by way of preface. We will now proceed to the discussion of the various branches of our subject, following in the main the order and mode of treatment adopted in past years.

General and Physical Chemistry of Minerals.

Mutual Relations of Fused Silicates or Salts.—The remarkable work of Day and Allen on the artificial production of plagioclase felspars [1] brought strong evidence from the synthetic side in favour of the view that these substances form a continuous series of mixed

[1] *Ann. Report*, 1905, 268.

crystals conforming to type I of Bakhuis Roozeboom's classification. These results, obtained by the study of heating and cooling curves, have been fully substantiated so far as the anorthite-labradorite portion of the series is concerned, by a series of experiments carried out by E. Dittler,[2] a member of Doelter's school. The preliminary notice of this investigation was referred to last year, and the detailed account is now before us. Eight mixtures of silica and alumina, with the carbonates of sodium and calcium, corresponding with felspars ranging from pure anorthite to $An_{65}Ab_{35}$, were melted and allowed to crystallise. The specific gravities and indices of refraction of the crystalline products were determined, and by means of a small electric furnace, combined with a microscope, the temperatures T_1 and T_2 were observed, at which the crystalline products became respectively, rounded at the edges, or changed into isotropic glass. The temperature T_3, at which crystallisation begins, and the final temperature of solidification, T_4, were also measured. These experiments differ from those of Day and Allen mainly in the method of determining the melting points, and whereas they state that anorthite melts sharply at 1532°, Dittler finds for the same substance $T_1 = 1290°$, $T_2 = 1370°$, $T_3 = 1300°$, $T_4 = 1180°$. Similar observations were made with mixtures containing potassium carbonate, and corresponding in composition with mixtures of orthoclase with anorthite, bytownite, and labradorite respectively. The principal conclusions arrived at are as follows. The presence of potash felspar favoured the production of zonal structure, the peripheral zones being most developed in the melts which contained least anorthite. From melts containing much anorthite and little orthoclase, anorthite containing potassium crystallised out, and the ground mass consisted of a mixture of the two components. On increasing the proportion of orthoclase, most of it solidified as glass. In the experiments with bytownite and labradorite, it was found that the miscibility of the two components increased with the increase in the sodium content, but for a given plagioclase the composition of the crystalline product remained practically the same however much orthoclase was added. From this it would appear that the plagioclases at the anorthite end of the series are only able to take up small quantities of orthoclase, not exceeding a few per cent. in the case of anorthite, and from 10 to 15 per cent. in the other felspars examined, while the molecules $KAlSi_3O_8$ and $NaAlSi_3O_8$ have the properties of isodimorphous substances, and are miscible.

Another research[3] undertaken in the same school has been

[2] *Tsch. Min. Mitt.*, 1910, **29**, 273.

[3] V. Haemmerle, *Jahrb. Min. Beil.-Bd.*, 1910, **29**, 719; *A.*, ii, 721.

prompted by the criticism directed against some of the earlier work on the interactions of fused silicates. It has been contended that the products obtained might be greatly influenced by the presence of impurities in the natural silicates employed. To meet this objection, a number of experiments have been carried out with mixtures of pure silica, magnesia, and aluminium hydroxide, with the carbonates of calcium and sodium. When mixtures corresponding with labradorite + diopside were fused, a number of minerals could be identified in the crystalline product, as, for example, diopside, soda-augite, aluminium-iron-augite, hedenbergite, labradorite, anorthite, magnetite, spinel, and hematite. Mixtures corresponding with olivine + labradorite + diopside gave similar results, and confirm the validity of the conclusions already arrived at by observations on natural minerals. Pure materials have likewise been employed by M. Hauke[4] in an investigation of a number of eutectic mixtures, in which the proportions of the compounds were calculated by means of Vogt's formula; the influence of magnesium chloride, of calcium chloride, and of tungstic acid in promoting crystallisation was also examined. Mixtures corresponding in composition with eutectics of anorthite + olivine, labradorite + olivine or diopside, oligoclase + enstatite, nepheline + diopside, and diopside + olivine were fused, and the order of crystallisation and the micro-structure of the products determined in each case. The application of the laws of eutectics to fused silicates has also been discussed by F. M. Flawitzky.[5] Whilst unable to agree with Vogt that the molecules of these silicates are not polymerised, he finds evidence in favour of the view that the degree of polymerisation is the same in each case.

Work of a similar character to that recorded above has been carried out in a number of other cases, and some of these may claim brief notice here. In the first place, the study of fused lead silicate has been continued,[6] and some interesting results have been obtained. The freezing-point curve suggests the existence of two eutectics and a maximum corresponding with Pb_2SiO_4. The first of these eutectics has, however, been shown to consist of two eutectics close together, with a maximum corresponding with the compound $3PbO,2SiO_2$. Another compound, $3PbO,SiO_2$, appears also to exist. Secondly, we may notice some work that has been done on the binary systems formed by calcium metasilicate with calcium chloride and calcium fluoride respectively.[7] In the former case, the eutectic point lies close to the calcium chloride point and

[4] *Jahrb. Min.*, 1910, i, 91 ; *A.*, ii, 510.
[5] *Nat. Phil. Soc. Imp. Univ. Kazan*, 1909 ; *A.*, ii, 510.
[6] S. Hilpert and R. Nacken, *Ber.*, 1910, **43**, 2565 ; *A.*, ii, 955.
[7] B. Karandéeff, *Zeitsch. anorg. Chem.*, 1910, **68**, 188 ; *A.*, ii, 954.

8° below it, whilst in the latter the eutectic point is at 1130° and corresponds with $48CaF_2$ and $52CaSiO_3$. Lastly, we may draw attention to two other investigations conducted on similar lines. The first of these deals with the relations of calcium sulphate to the alkaline sulphates,[8] whilst in the second the relations of the sulphate of sodium to its fluoride and chloride are discussed,[9] as well as the behaviour of the simple ternary system, composed of all three. The normal sulphates of potassium, rubidium, and cæsium are enantiotropic-dimorphic, being orthorhombic at the ordinary temperature, and hexagonal above the transition temperatures, which are 580°, 649°, and 660° respectively. The temperature-concentration diagrams of each of these salts, when mixed with calcium sulphate, have been examined, as well as the systems composed of calcium sulphate and lithium or sodium sulphates. Potassium sulphate forms the enantiotropic-dimorphic double salt, $K_2SO_4,2CaSO_4$. Compounds of similar composition are obtained with rubidium and cæsium, the former being trimorphous, the latter dimorphous. Sodium sulphate gives a double salt, $4Na_2SO_4,CaSO_4$, completely miscible with sodium sulphate. Glauberite, $Na_2SO_4,CaSO_4$, cannot be obtained from fusions, a melt of the proper composition solidifying as a eutectic of anhydrite, $CaSO_4$, with mixed crystals of $4Na_2SO_4,CaSO_4$ and $CaSO_4$. Lithium sulphate forms neither double salts nor mixed crystals with calcium sulphate.

Constitution of Silicates.—Tschermak's method of determining the constitution of silicates by studying the dehydration of the silicic acids prepared from them continues to give rise to discussion. Tschermak [10] himself claims to have shown that the vapour tension method of detecting discontinuities in the velocity of dehydration yields results similar to those obtained by the dynamic method, although the latter is to be preferred. On the other hand, it is maintained [11] that the concentration and temperature of the hydrochloric acid used to decompose the silicate and the temperature at which the silicic acid is dried have an important influence on the result, and it has been shown that the composition of the silicic acid obtained from leucite varied between $H_{10}Si_6O_{17}$ and $H_6Si_2O_7$.

Electrical Conductivity of Minerals.—As the result of an elaborate investigation into the electrical conductivity of minerals both in the crystalline and fused conditions, C. Doelter [12] classifies these substances as follows: (A) Those which exhibit metallic con-

[8] H. Müller, *Jahrb. Min. Beil.-Bd.*, 1910, **30**, 1 ; *A.*, ii, 776.

[9] A. Wolters, *ibid.*, 55 ; *A.*, ii, 775.

[10] *Zeitsch. anorg. Chem.*, 1910, **66**, 199 ; *A.*, ii, 407.

[11] A. Serra, *Atti R. Accad. Lincei*, 1910, [v], **19**, i, 202 ; *A.*, ii, 407.

[12] *Monatsh.*, 1910, **31**, 493 ; *A.*, ii, 818.

ductivity at all temperatures without electrolytic conductivity, such as galena, antimonite, ilmenite, pyrite, magnetite. (B) Crystals which are insulators at the ordinary temperature, but which exhibit metallic conductivity at rather higher temperatures, for example, blende, molybdenite, fahlerz. (C) Crystals such as cassiterite and chrysoberyl, which probably exhibit both metallic and electrolytic conductivity, but in which polarisation has not been definitely determined. (D) Crystals which are insulators at the ordinary temperature, but become conductors and exhibit polarisation at high temperatures. These include barytes, sapphire, many silicates, and metallic chlorides and iodides. The transition from the amorphous to the crystalline state is usually accompanied by a break in the temperature-conductivity curve. In the case of polymorphous substances, the form stable at high temperatures is the best conductor.

Chemical Crystallography.

In any historical survey of the development of our ideas concerning the relation between chemical constitution and crystalline form, the year 1910 must always stand out prominently as associated with two important events. In the first place, the publication of the third volume of Groth's invaluable *Chemische Krystallographie* has reduced to order and presented in a form convenient for study all available data concerning crystals of derivatives of the paraffin, olefine, and acetylene series, as well as those of uric acid, the terpenes, and *cyclo*hexane. Secondly, the Barlow-Pope theory has been successfully applied to the solution of the problems presented by the aliphatic hydrocarbons, and it has been shown that, so far as the somewhat meagre crystallographic data allow of comparison, the results deduced from the theory are in harmony with the goniometric observations.[13]

As is well known, this theory rests on a very few simple assumptions. In the first place, each atom of the molecules under consideration is believed to possess its own sphere of influence; the spheres of influence of atoms of the same kind are to be regarded as equal in a set of compounds belonging to the same series, while the spheres of influence of atoms of different kinds are proportional to the fundamental valencies of the atoms; thus, the sphere of influence of the carbon atom is four times as great as that of the hydrogen atom. Secondly, for the purposes of this discussion, these spheres of influence may be represented by means of incompressible, but deformable, material spheres of appropriate sizes, piled together in regular order according to the principles of

[13] W. Barlow and W. J. Pope, *Trans.*, 1910, **97**, 2308.

closest-packing. Now, since the crystalline forms of the hydrocarbons themselves are unknown, the results developed from the theory can only be tested by means of their halogen or other derivatives. The halogens are, however, univalent, like hydrogen. Their spheres of influence are therefore, ex hypothesi, approximately equal in size to those occupied by hydrogen atoms, and in the closely-packed assemblages of material spheres which represent the various molecules, hydrogen spheres ought to be capable of substitution by others of about the same size, representing chlorine, bromine, or iodine, without destroying the character of the assemblage. In the first section of the paper before us, it is shown that such an assumption does no violence to the crystallographic data in cases where direct comparison is possible, and that we are therefore justified in drawing conclusions as to the structure of the hydrocarbons from the study of the morphology of their halogen derivatives. In the next section, the structure of methane is considered. Starting with a number of equal spheres representing carbon regularly arranged in closest-packing, it is shown how half the spheres may be removed in a regular manner, and the interstices thereby left in the structure may be filled with groups of four hydrogen spheres, each having one-quarter of the volume of a carbon sphere, so that the whole assemblage remains highly symmetrical and closely packed. This assemblage has not merely the composition of methane, but is so far in accord with the van't Hoff—Le Bel theory that the units into which the whole structure may be apportioned each consists of a carbon sphere with four hydrogen spheres, arranged round it in such fashion that the centre of each of the latter lies approximately at the corner of a regular tetrahedron. The structure thus arrived at is found to be in harmony with the crystalline forms of carbon tetraiodide, carbon tetrabromide, iodoform, and of tetrabromo-$\beta\beta$-dimethylpropane. The structure of methane once settled, the next problem is to account for its normal homologues. Now, since any normal paraffin may be represented as $H\cdot[CH_2]_n\cdot H$, it is desirable, in the first instance, to determine the structure of the general methylene assemblage of the empirical composition CH_2, for by addition to it of hydrogen spheres in appropriate number and in regular arrangement the structure of any other normal paraffin can be deduced. A simple method of constructing the methylene assemblage is the following. Space is regarded as divided into a series of endless hexagonal prisms; these are further sub-divided into hexagonal cells by planes perpendicular to the prism axes, the height of each cell being equal to its shortest diameter. In each cell is placed a sphere representing a carbon atom, and at each cell corner is placed a smaller sphere representing

the hydrogen atom, and touching the six neighbouring carbon spheres. The assemblage, which has the empirical composition CH_2, is next adjusted by increasing the diameters of the small spheres until their volumes are one-quarter those of the large spheres. After the further adjustment required to reduce the assemblage, dislocated by the last operation, to the state of closest-packing, a structure is arrived at which is in harmony with the stereochemical features of the chain CH_2. From the methylene assemblage the structure proper to ethane can readily be obtained by inserting pairs of hydrogen spheres in a symmetrical manner. The crystallographic properties of the hexahalogen derivatives of ethane are in accord with the structure so obtained. If the adjustment of the hexagonal cell assemblage of empirical composition CH_2 is carried out in a slightly different way, an alternative methylene assemblage is attained, which exhibits tetragonal symmetry, and from which normal butane may be derived. It is found, moreover, that the crystallographic properties of the homologues of ethane can readily be brought into relation with one or other of the methylene assemblages.

To bring the secondary and tertiary paraffins within the scope of the theory is now a comparatively simple task. Thus, to arrive at tetramethylmethane, we have merely to remove symmetrically every fourth group of four hydrogen spheres from a methane assemblage, and replace them by an equivalent carbon atom. This can be done in two ways, the resulting assemblages having cubic or tetragonal symmetry respectively. The observation that the crystals of the compound $C(CH_2Br)_4$ are pseudo-cubic affords strong confirmation of the validity of this procedure. By removing methylene layers from tetramethylmethane, we arrive at trimethylmethane, $CH(CH_3)_3$, and by the re-insertion of such layers in appropriate positions, *iso*pentane, $(CH_3)_2CH{\cdot}CH_2{\cdot}CH_3$, can be accounted for. The assemblage representing propane can also be easily derived from that assigned to tetramethylmethane. Now, since the graphic formulæ for all the remaining hydrocarbons of the form C_nH_{2n+2} can be derived from those of methane, trimethylmethane, and tetramethylmethane by the insertion of methylene groups, and as by a similar process the assemblages proper to the various hydrocarbons can be constructed from those which represent the structures of the simpler ones, it follows that the geometrical method of interpreting molecular structure is in harmony with the facts already summarised in our ordinary chemical formulæ.

The structure of the paraffins once established, it is an easy step to the type of assemblage characteristic of the olefines.

Starting with the methylene assemblage in its tetragonal form, we remove the small spheres representing hydrogen from one face of each of two composite layers, and then key together the faces laid bare. This process is the geometrical representation of the production of an ethylene linking. On adding to this assemblage hydrogen or halogen spheres in suitable numbers, ethylene or its halogen derivatives are made. The crystals of the compound C_2I_4 have constants consistent with this structure. On passing next to the homologues of ethylene, it can be shown that structures corresponding with all possible molecules of the formula C_4H_8 can easily be obtained. Of these molecules there are six. The first three, namely, *cis-s*-dimethylethylene, *trans-s*-dimethylethylene, and ethylethylene, can all be derived by applying in different ways to the normal butane assemblage the process of excising hydrogen, which led to the production of ethylene. From the *iso*butane assemblage a fourth arrangement, representing *as*-dimethylethylene, can be obtained. Another assemblage, that of methyltrimethylene, can be obtained from both butane and from *iso*butane, and the sixth, that of tetramethylene, can be made from butane only. Our knowledge of the crystallography of substances of this kind is lamentably deficient, and it will be the work of the future to fill in the details of the scheme of which the main outlines have now been clearly traced. Little, too, is known about the crystals of acetylene derivatives, but the structure of acetylene may be arrived at thus. Starting with a closest-packed assemblage of equal carbon spheres of volume four, place in each cavity surrounded by six large spheres a smaller sphere representing hydrogen, and touching each of its larger neighbours. These small spheres are just as numerous as the large ones, but their volumes are less than unity. Let them therefore expand until their volumes become unity, and adjust the dislocated assemblage so that each large sphere is in contact with one other sphere of its own size, the points of contact of sphere with sphere being distributed through space as evenly as possible. From this assemblage, which represents acetylene, those of allylene and ethylacetylene can easily be obtained. This simple method of representing the structure of acetylene is further remarkable in that by its aid the transformation of acetylene into aromatic hydrocarbons can be accounted for, it being only necessary slightly to distort the acetylene assemblage to bring it into the configuration proper to benzene. The behaviour of di-iodoacetylene, which, by slight warming or by the action of light, is converted into hexaiodobenzene, is in accord with this, and certain other similar cases of polymerisation receive the same explanation.

No one who carefully studies this paper can fail to be convinced

that it marks a notable advance, and that there is every prospect that in the near future the correlation of chemical constitution and crystal form will proceed rapidly and surely along the lines here indicated.

The validity of the conclusions derived from the Barlow-Pope theory can only be properly tested by means of accurate data obtained for series of related substances; for the present, at any rate, isolated observations are of minor value. We will therefore now consider a few researches of the kind on which future progress depends. For a number of years past, H. E. Armstrong[14] has been accumulating observations on derivatives of benzene. The inquiry has embraced a wide field, and included chlorides and bromides of the various dihalogen substitution products of benzenesulphonic acid. Some remarkable relations have been detected, and the study of a long series of compounds containing two halogen atoms in the para-position has been completed.[15] The results of accurate measurements made on twenty-nine different derivatives show that all belong to two crystalline types, one derived from the hexagonal, and the other from the cubic mode of close-packing of equal spheres. In each the carbon atoms appear to be arranged exactly as in crystalline benzene, and the introduction of substituting atoms or groups merely expands the benzene assemblage in two of the three possible directions, the orthorhombic symmetry of the benzene assemblage being usually lowered in the process.

A large number of derivatives of ethylenediamine have been examined by M. Frank,[16] and some more or less isolated observations have been published by F. Zambonini[17] and by C. Blass.[18]

Of greater importance is a memoir[19] which has for its object the study of the relations between density and refractive index in the case of a number of crystalline, isomeric or polymeric, organic substances; thus, methyl oxalate has been compared with succinic acid, catechol with resorcinol and quinol, whilst the relations due to polymerisation have been studied in the case of dicyanodiamide, $(CN{\cdot}NH_2)_2$, and melamine, $(CN{\cdot}NH_2)_3$. The chief result of this elaborate investigation is to confirm the validity of the law discovered by Landolt from a study of isomeric organic liquids, namely, that the grouping of the atoms in the molecules of metameric substances has very little influence on the refractivity, and that therefore the members of a metameric group possess nearly

14 *Trans.*, 1910, **97**, 1578.
15 R. T. Colgate and E. H. Rodd, *ibid.*, 1585.
16 *Zeitsch. Kryst. Min.*, 1910, **47**, 346; *A.*, i, 302.
17 *Ibid.*, 620; *A.*, ii, 610.
18 *Ibid.*, **48**, 20; *A.*, i, 614.
19 K. Heydrich, *ibid.*, **48**, 243; *A.*, i, 705.

the same specific refractivity. Further, it would appear that the variations in specific refractivity occurring in the case of polymeric substances are much greater than those observed in the case of metamerides, the denser substance having always the smaller specific refractivity. The application of this law to minerals indicates that calcite and aragonite are polymerides, but that the three varieties of titanium dioxide are metameric, while of the three silicates of the formula Al_2SiO_5, andalusite and cyanite are to be regarded as metamerides, but fibrolite is a polymeric form. It has further been found that intimate morphotropic relations exist between the two dinitrotoluenes ($CH_3 : NO_2 : NO_2 = 1 : 2 : 4$ and $1 : 2 : 6$) and between dicyanodiamide and melamine, whilst the two compounds, $C_6H_4(OH)\cdot SO_3K,2H_2O$ ($OH : SO_3K = 1 : 2$) and $C_6H_4(OH)\cdot SO_3K$ ($OH : SO_3K = 1 : 4$), curiously enough, exhibit the same optical relations as normal position isomerides.

The relations between thallium and the alkali metals have been further elucidated by A. E. H. Tutton,[20] who has subjected the double sulphate and selenate of thallium and zinc to crystallographic and optical examination in his accustomed thorough manner. He finds that the properties of these salts justify their inclusion in the isomorphous series of the type $R_2M\left\{{S \atop Se}O_4\right\}_2,6H_2O$, but that they must not be brought into the more exclusive eutropic series within the isomorphous group.

Some interesting observations on the crystallography of the mercury halides have been published by J. S. van Nest.[21] Mercuric chloride, he finds, is dimorphous, possessing two orthorhombic modifications, the first proper to the pure salt, the second a form isomorphous with that of mercuric bromide. The chloride and bromide form an interrupted mixed series, and a double salt probably exists. The bromide is trimorphous, for in addition to entering into mixed crystals of the form of the chloride, it will also crystallise with the red tetragonal form of the iodide. Like the chloride, the latter is dimorphous, being isomorphous in its yellow form with the orthorhombic bromide.

The position of silicon in the periodic classification is such as to suggest the existence of analogies between the crystal forms of compounds of silicon and of carbon. Compounds of the two elements of analogous composition are, however, very different in form, and G. Jerusalem[22] has sought to explain the discrepancy in the light of the Barlow-Pope theory by the suggestion that, whereas the fundamental valency of carbon is four, that of silicon is but

[20] *Proc. Roy. Soc.*, 1910, **83**, A, 211; *A.*, ii, 127.
[21] *Zeitsch. Kryst. Min.*, 1910, **47**, 263; *A.*, ii, 295.
[22] *Trans.*, 1910, **97**, 2190.

two. He has shown that the morphotropic relations existing between silicon and carbon compounds, such as $(C_6H_5\cdot CH_2)_3Si\cdot OH$ and $(C_6H_5\cdot CH_2)_3C\cdot OH$, can be readily accounted for on this hypothesis.

In concluding this section, we may call attention to some remarkable observations which have recently been made on the crystals of potassium silicotungstate. It has, up to the present, been generally believed that the two enantiomorphous forms assumed by substances, such as quartz and sodium chlorate, are alike in everything save in the sign of the rotation produced in the plane of polarisation of light traversing the crystals. There appear, however, to be indications of the existence of more profound differences. Thus, it has been known for some time that potassium silicotungstate crystallised from aqueous solution almost invariably appears in the right-handed form. This curious fact has not only been verified by H. Copaux,[23] but he has also shown that, although the left-handed form can be obtained, it is produced more slowly and dissolves more rapidly than its enantiomorph. When sodium chlorate was examined, it was found, contrary to the observations of previous experimenters, that there was a tendency for right-handed crystals to preponderate, and the velocity of growth of these appears to be distinctly greater than is the case with left-handed crystals. Hence he concludes that the two enantiomorphous forms exhibited by such substances are not to be considered identical, but rather as dimorphous, and it is therefore conceivable that a substance might exist exhibiting rotatory power, but invariably appearing in one form, the other being quite unstable. These observations and the conclusions based on them have also been discussed by E. Sommerfeldt.[24]

New Minerals.

Anemousite, Barbierite, Carnegieite.—As these three names have been applied by American investigators to different varieties of felspar, it will be convenient to consider them together. Anemousite is found in large, clear crystals, well suited for chemical and optical determination, in the basaltic lava of the island of Linosa, and has been the subject of a most careful examination by H. S. Washington and F. E. Wright.[25] The physical characters of the mineral indicate a plagioclase, Ab_6An_4 to Ab_5An_4, but the results of analyses cannot be explained by any mixture of albite and anorthite, though they are expressed pretty accurately by the formula

$$Na_2O,2CaO,3Al_2O_3,9SiO_2 \text{ or } (\tfrac{1}{3}Na_2,\tfrac{2}{3}Ca)Al_2Si_3O_{10},$$

part (about 1/12) of the sodium being replaced by potassium. To

[23] *Bull. Soc. franç. Min.*, 1910, **33**, 162; *A.*, ii, 301.
[24] *Tsch. Min. Mitt.*, 1910, **29**, 353.
[25] *Amer. J. Sci.*, 1910, [iv], **29**, 52.

explain this discrepancy, Washington and Wright assume the existence of a soda-anorthite molecule, $Na_2Al_2Si_2O_8$, and show that the composition and properties of the Linosa felspar can be satisfactorily accounted for if it be regarded as a mixture of albite, anorthite, and soda-anorthite in about the proportions 8 : 10 : 1. This peculiar felspar they propose to call *anemousite*, from the old Greek name of the island of Linosa, whilst for soda-anorthite they suggest the name *carnegieite*, for although present in but small proportion in anemousite, it has been prepared artificially in the Geophysical Laboratory at Washington, and its individuality, as a triclinic felspar allied to anorthite, satisfactorily established. The existence of a monoclinic felspar, $NaAlSi_3O_8$, isomorphous with orthoclase and dimorphous with albite, appears also to have been demonstrated, largely owing to the analytical work of P. Barbier,[26] and the name *barbierite* has therefore been suggested for this species.[27] The felspar from Kragerö, containing but 1·15 per cent. of K_2O, is almost pure barbierite, and a soda-sanidine from Mitrowitza consists approximately of equal parts of orthoclase and barbierite.[28] It occurs in large, monoclinic crystals, the cleavage angle, PM, being 90°1′. The extinction on P is 0°, and on M, 2°52′. The optic axial plane is perpendicular to the plane of symmetry, and an acute negative bisectrix emerges through P. $2E = 37°55′$. The composition may be expressed as $8KAlSi_3O_8 + 9NaAlSi_3O_8$.

Cobaltocalcite.—A red variety of calcite occurs at Capo Calamita, Elba.[29] It is denser and harder than ordinary calcite, and contains 2 per cent. of cobalt carbonate.

Gageite.—A new mineral occurring in delicate, colourless, acicular crystals has been found at Franklin, New Jersey, associated with calcite, zincite, willemite, and leucophœnicite.[30] An analysis made on 0·04 gram shows that it is a hydrated silicate of manganese, magnesium, and zinc of the general formula $8RO,3SiO_2,2H_2O$. It is therefore closely related to the leucophœnicite on which it is implanted, and probably shares with it a common origin.

Goldfieldite.—At the Mohawk mine in the goldfield mining district of Nevada, some gray material has been met with, which is believed to be a cupric sulphantimonite, in which part of the antimony is replaced by arsenic and bismuth, and much of the sulphur by tellurium.[31] The formula assigned is

$$5CuS,(Sb,Bi,As)_2(S,Te)_3,$$

26 See *Ann. Report*, 1909, 211.

27 W. T. Schaller, *Amer. J. Sci.*, 1910, [iv], **30**, 358 ; *A.*, ii, 1078.

28 F. Angel, *Jahrb. Min. Beil.-Bd.*, 1910, **30**, 254 ; *A.*, ii, 783.

29 F. Millosevich, *Atti R. Accad. Lincei*, 1910, [v], **19**, i, 91 ; *A.*, ii, 221

30 A. H. Phillips, *Amer. J. Sci.*, 1910, [iv], **30**, 283 ; *A.*, ii, 968.

31 F. L. Ransome, *United States Geol. Surv.*, *Prof. paper*, No. 66.

but as the analysis shows a very high summation, and was made on a small quantity of the substance, which exhibited no crystalline form, the individuality of the species can hardly be considered as established beyond question.

Joaquinite.—This name has been proposed for minute orthorhombic crystals found in the natrolite vein in which benitoite occurs in California. The crystals are honey-yellow or light brown in colour, and contain silica, titanium, calcium, and iron, but they have not as yet been completely determined.[32]

Minguetite.—Opaque black or greenish-black plates occur in aggregates associated with chalybite, quartz, and some galena in a vein at the junction of beds of magnetite with an altered diorite in the Minguet mine, near Segré, France.[33] The substance was formerly believed to be biotite, but on analysis was found to contain too little alumina and alkalis, and to give up its water too easily. The formula, $17SiO_2,4(Fe,Al)_2O_3,8(Fe,Mg)O,K_2O,8H_2O$, indicates that in composition the mineral is intermediate between the mica, lepidomelane, and the chlorite, stilpnomelane.

Mosesite.—In these reports for 1906 and 1907, attention was directed to the remarkable mercury minerals found at Terlingua, Texas, and the discovery of another member of the series has now to be recorded.[34] The new mineral, for which the name mosesite has been proposed, somewhat resembles kleinite, being apparently a mercury ammonium compound containing chlorine and sulphate, the mercury being probably in the mercurous condition. It occurs on calcite in minute, regular octahedra or in spinel-twins. The crystals are canary-yellow in colour, and birefringent. On heating to 186°, they become isotropic, but revert slowly to the birefringent condition on cooling.

Pilbarite.—A bright yellow, ochreous mineral occurs in a tantalite lode at Wodgina, Pilbara Goldfield, Western Australia.[34a] It is amorphous, and probably a hydrous pseudomorph. The composition is approximately expressed by the formula:

$$PbO,UO_3,ThO_2,2SiO_2,2H_2O+2H_2O.$$

Quercyite.—A study of the mineralogical constitution of the French phosphorites has led A. Lacroix [35] to suggest a new nomenclature for these substances. Isotropic compounds of calcium phosphate and carbonate are classed as colophanites, whilst mixtures

[32] G. D. Louderback, *Bull. Dept. Geol. Univ. California*, 1909, **5**, 331; *A.*, ii, 310.

[33] A. Lacroix, *Bull. Soc franç. Min.*, 1910, **33**, 270; *A.*, ii, 783.

[34] F. A. Canfield, W. F. Hillebrand, and W. T. Schaller, *Amer. J. Sci.*, 1910, [iv], **30**, 202; *A.*, ii, 965.

[34a] E. S. Simpson, *Chem. News*, 1910, **102**, 283.

[35] *Compt. rend.*, 1910, **150**, 1213; *A.*, ii, 720.

of colophanite with optically negative crystalline matter of similar composition are termed quercyite. Sometimes the crystalline matter mixed with the colophanite is partly positive, partly negative. In this case the mixture is termed β-quercyite.

Samsonite.—Steel-grey, monoclinic crystals, which resemble miargyrite in appearance, have been found at the Samson mine, St. Andreasberg, associated with pyrargyrite, galena, pyrolusite, etc.[36] On analysis, the formula was found to be $2Ag_2S,MnS,Sb_2S_3$.

New Vanadate.—A vanadate, somewhat resembling cupro-descloizite in composition, has been observed in the cupriferous deposits of Bena (d)e Padru, near Ozieri, Sardinia.[37]

Wiltshireite.—This name has been assigned by W. J. Lewis [38] to a mineral found in the dolomite of the Binnenthal, where it occurs in small, monoclinic crystals having a somewhat characteristic lustre and the following crystallographic constants: $a:b:c = 1·587:1:1·070$, $\beta = 79°16'$. The chemical composition has not yet been determined owing to paucity of material, but the individuality of the species is inferred from the crystallographic characters. The same substance appears to have been noted by R. H. Solly [38a] in 1903, and is referred to under the title of rathite α in the list of minerals from Binn given by L. Desbuissons in his book, *La Vallée de Binn.*

Mineral Analyses.

Adamite.—Pure material from Thasos, Turkey, has a composition agreeing very closely with the usual formula, $Zn_3As_2O_8,Zn(OH)_2$.[39] The axial ratios of the orthorhombic crystals are $a:b:c = 0·9764:1:0·7049$.

Alexandrite.—This variety of chrysoberyl possesses the remarkable property of appearing dark green in daylight, but cherry-red in artificial light. It has been found that solutions of chromium sulphate which have been gently boiled exhibit the same phenomena, and it seems probable that the peculiar properties of the gem are due to the presence of chromium oxide, partly in colloidal solid solution, and partly in isomorphous admixture.[40]

Alstonite.—The occurrence of this rare mineral has been reported from the New Brancepeth Colliery, near Durham, where it is found associated with barytes and witherite in a fault-vein intersecting

[36] Werner and Fraatz, *Centr. Min.*, 1910, 331 ; *A.*, ii, 620.
[37] D. Lovisato, *Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 326 ; *A.*, ii, 1077.
[38] *Phil. Mag.*, 1910, [vi], **20**, 474.
[38a] *Nature*, 1903, **69**, 142.
[39] V. Rosický, *Bull. Intern. Acad. Sci. Bohême*, 1909, **13**, 21 ; *A.*, ii, 309.
[40] O. Hauser, *Zeitsch. angew. Chem.*, 1910, **23**, 1464 ; *A.*, ii, 873.

the coal measures.[41] An analysis agrees approximately with the formula $BaCa(CO_3)_2$. Sp. gr = 3·67.

Amphibole Group.—X. Galkin [42] has analysed seven specimens of hornblende crystals from different localities in the Rhön Mountains. The composition is nearly the same in each case, the mean values being as follows:

SiO_2.	TiO_2.	P_2O_5.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	Na_2O.	K_2O.	H_2O
40·65	3·76	0·88	13·87	8·36	4·57	12·34	12·23	2·27	1·14	0·45

The part played by the titanium and the general relation of these results to the views as to the composition of hornblende held by Tschermak, Scharizer, Rosenbusch, and Penfield are discussed at length, but no very definite conclusions are reached.

Antlerite.—A basic copper sulphate, $3CuSO_4,7Cu(OH)_2$, was described under this name by Hillebrand in 1889. Ten years later the name stelznerite was assigned by Arzruni and Thaddéeff to a mineral from Chili, for which they found the formula $CuSO_4,2Cu(OH)_2$. Optical examination of the type specimen of antlerite and comparison of its composition with that of stelznerite has convinced W. T. Schaller [43] that the two substances are identical, and that the formula assigned to stelznerite is correct. He proposes, however, to abandon the latter name, in view of the prior use of the term antlerite.

Apophyllite.—Pure material from the Radauthal, Harz Mountains, has approximately the formula $4Ca_2H_6Si_3O_{11},K_2H_8Si_3O_{11}$. The specimen is remarkable in that it appears to contains alumina (1·78 per cent.) as an essential constituent.[44]

Arsenopyrite.—Brilliant crystals from Franklin Furnace, New Jersey, have a composition accurately expressed by the formula FeAsS, part of the iron being replaced by 1·16 per cent. of cobalt.[45]

Atacamite.—The composition of remarkable twinned crystals from Collahurasi, Chili, was found on analysis to agree very closely with the formula $CuCl_2,3Cu(OH)_2$.[46]

Axinite.—A specimen from the Radauthal [47] is nearly pure manganese axinite of the formula $HMnCa_2BAl_2Si_4O_{16}$, and agrees with the general formula $HR^{II}R^{II}_2BAl_2Si_4O_{16}$ proposed by Rammelsberg for the mineral from Bourg d'Oisans. The same general formula covers the case of crystals from Moosa Cañon, San Diego County, California, for which the composition

$$8SiO_2,2Al_2O_3,2(Fe,Mn,Mg)O,4CaO,H_2O,B_2O_3$$

[41] L. J. Spencer, *Min. Mag.*, 1910, **15**, 302; *A.*, ii, 307.
[42] *Jahrb. Min. Beil.-Bd.*, 1910, **29**, 681; *A.*, ii, 721.
[43] *Amer. J. Sci.*, 1910, [iv], **30**, 311; *A.*, ii, 1076.
[44] J. Fromme, *Tsch. Min. Mitt.*, 1909, **28**, 305; *A.*, ii, 314.
[45] C. Palache, *Amer. J. Sci.*, 1910, [iv], **29**, 177; *A.*, ii, 219.
[46] W. E. Ford, *ibid.*, **30**, 16.
[47] J. Fromme, *Tsch. Min. Mitt.*, 1909, **28**, 305; *A.*, ii, 314.

has been found by W. T. Schaller.[48] From the consideration of other analyses, he has been led to suggest that the atomic proportion of calcium is constant, and that manganese and ferrous iron replace one another isomorphously, the mineral being regarded as an isomorphous mixture of ferroaxinite, $HFeCa_2BAl_2Si_4O_{16}$, and manganoaxinite, $HMnCa_2BAl_2Si_4O_{16}$. Small, transparent crystals from the Consumes copper mine in Amador County also afforded results in harmony with these conclusions.

Baddeleyite.—This mineral occurs in some quantity in Brazil, and its composition has been investigated by E. Wedekind,[49] and also by L. Weiss and R. Lehmann.[50] From this work it appears that the Brazilian specimens consist in the main of dioxide of zirconium, together with small amounts of ferric oxide, alumina, silica, and water. Traces of titanium are also present. The zirconia separated from large quantities of the material was submitted to an elaborate process of fractionation by Weiss and Lehmann, but no indications of resolution into two or more oxides could be observed. Similar results were obtained by O. Hauser and F. Wirth,[51] who fractionated the zirconia prepared from a number of minerals to see if they could find any evidence for the existence of the so-called euxenium earth of Hofmann and Prandtl.[52] The results were negative.

Barytocelestine.—The mineral described under this name from the Binnenthal has been shown to be pure barytes.[53] Barytocelestine does not appear to exist in distinct crystals, and the specimens from other localities are probably mixtures.

Bementite.—The occurrence of this mineral at Franklin Furnace, New Jersey, has enabled a fresh investigation of its characters to be made.[54] It crystallises in the orthorhombic system, has the formula $H_6Mn_5(SiO_4)_4$, and is closely related to tephroite.

Bertrandite.—Crystals of this rare mineral resulting from the weathering of beryl occur in the Altai Mountains.[55] The composition is represented by the formula $H_2Gl_4Si_2O_9$, although the amount of glucinum found is rather low.

Beryl.—The composition of pink beryls from Madagascar and from Mesa Grande and Pala, both in San Diego County, California, has been studied by W. E. Ford,[56] who has compared their optical

[48] *Zeitsch. Kryst. Min.*, 1910, **48**, 148 ; *A.*, ii, 874.
[49] *Ber.*, 1910, **43**, 290 ; *A.*, ii, 218.
[50] *Zeitsch. anorg. Chem.*, 1909, **65**, 178 ; *A.*, ii, 133.
[51] *Ber.*, 1910, **43**, 1807 ; *A.*, ii, 713. [52] *Ibid.*, 1901, **34**, 1064 ; *A.*, 1901, ii, 387
[53] V. Rosický, *Bull. Intern. Acad. Sci. Bohême*, 1909, **13**, 21 ; *A.*, ii, 309.
[54] C. Palache, *Amer. J. Sci.*, 1910, [iv], **29**, 182 ; *A.*, ii, 219.
[55] P. P. Pilipenko, *Bull. Acad. Sci. St. Pétersbourg*, 1909, 1116 ; *A.*, ii, 48.
[56] *Amer. J. Sci.*, 1910, [iv], **30**, 128 ; *A.*, ii, 873.

properties with those of beryls rich in alkalis from Willimantic, Conn., and from Hebron, Maine, analysed by Penfield and by Wells. It is found that as the glucina is replaced by alkalis there is an increase in the values of the refractive indices, birefringence, and specific gravity, as exhibited in the following table:

Locality.	ω.	ϵ.	Sp. gr.	Li_2O.	Na_2O.	K_2O.	Cs_2O.
Mesa Grande ...	1·58157	—	2·714	0·46	0·84	0·18	—
Willimantic......	1·58455	1·57835	2·730	0·28	0·75	0·12	—
Pala	1·59239	1·58488	2·785	1·33	1·59	0·28	0·57
Madagascar	1·59500	1·58691	2 790	1 68	1·60	—	1·70
Hebron	1·59824	1·59014	2·800	1·60	1·13	—	3·60

Lacroix [57] has pointed out that the beryls rich in cæsium from Madagascar are similar to those from the Ural Mountains recently described by Vernadsky under the name vorobyevite.[58] The beryls of Madagascar have also been the subject of a somewhat elaborate investigation by L. Duparc and his assistants,[59] who have obtained the following values for the indices of refraction and specific gravities:

Locality.	Colour.	Sp. gr.	ω.	ϵ.
Tsilaisina	pink	2·7165	1·5830	1·5747
Tsaravovona	,,	2·7027	1·5782	1·5725
Antaboko	blue	2·7477	1·5897	1·5819
Tetehina........	,,	2·7116	1·5818	1·5748
Ambatolampy	,,	2·7192	1·5838	1·5752
Tongafeno	,,	2·7379	1·5849	1·5771

The composition of the crystals from Tsilaisina was as follows:

SiO_2.	Al_2O_3.	GlO.	MnO.	Li_2O.	Na_2O.	K_2O.	H_2O.
64·76	18·14	13·76	0·003	0·04	0·73	0·15	2·24

P. Barbier and F. Gonnard [60] have found that beryls from pegmatite near Biauchaud, Puy-de-Dôme, and from Montjeu can be represented by the formula $H_2Gl_5Al_4Si_{11}O_{34}$.

Bismite occurs as the result of the oxidation of bismuth sulphide in colourless scales at several mines in Nevada.[61] The scales are of hexagonal outline, and possess basal cleavage. They exhibit a negative uniaxial interference figure, and probably belong to the rhombohedral system. Analysis of material mixed with much gangue indicates that the substance is either bismite, Bi_2O_3, or hydrous bismuth oxide.

Bityite.—The following revised formula has been assigned to this rare mineral [62]:

$$21SiO_2,16Al_2O_3,14(Ca,Gl,Mg)O,4(Li,Na,K)_2O,14H_2O.$$ [63]

[57] *Bull. Soc. franç. Min.*, 1910, **33**, 44; *A.*, ii, 307.

[58] See *Ann. Report*, 1909, 228.

[59] *Bull. Soc. franç. Min.*, 1910, **33**, 53; *A.*, ii, 312.

[60] *Ibid.*, 74, 78; *A.*, ii, 418.

[61] W. T. Schaller and F. L. Ransome, *Amer. J. Sci.*, 1910, [iv], **29**, 173; *A.*, ii, 220.

[62] A. Lacroix, *Bull. Soc. franç. Min.*, 1910, **33**, 52; *A.*, ii, 307.

[63] Compare *Ann. Report*, 1909, 222.

Brochantite.—The composition of good crystals from Collahurasi, Chili, is accurately represented by the formula $CuSO_4,3Cu(OH)_2$.[64]

Bröggerite.—The composition of iron-black radioactive crystals from Borneo may be represented as:

$$4SiO_2,45UO_3,48UO_2,12PbO,6ThO_2,2Y_2O_3,CaO,4FeO,9H_2O.$$[65]

Carnotite.—An investigation of the yellow powder occurring in crevices in an intimate mixture of ilmenite, rutile, and magnetite at Radium Hill, South Australia, has led to the conclusion that this substance is a definite mineral species, essentially a hydrated vanadate of uranium and potassium.[66] The minute orthorhombic plates have a good basal cleavage, perpendicular to which an acute negative bisectrix emerges. Incidentally it has been shown that the matrix in which the carnotite is found, and to which the names davidite and sefströmite have been applied, is a mixture.

Cordierite.—Fragments of this mineral from the micaceous quartzite of the Ibity Mountains, Madagascar, have the following composition [67]

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	ign.	Total.	Sp. gr.
49·05	33·08	0·83	4·38	11·04	1·64	100·02	2·5933

The refractive indices are $\alpha = 1·53958$, $\beta = 1·54516$, $\gamma = 1·54853$.

Cuspidine.—This interesting species, hitherto only recorded from Vesuvius, occurs also at Franklin Furnace, New Jersey, for white crystal fragments from the Parker Shaft were found on analysis to have the formula $Ca_2Si(O,F_2)_4$.[68]

Dahllite.—A mineral exhibiting the characteristic scroll structure discovered in calcedonite by Lévy, and imitated by Wallerant in organic compounds by melting them in the presence of optically active substances, occurs in the phosphorites of Mouillac.[69] The composition of the substance is practically identical with that of dahllite, $2Ca_3P_2O_8,CaCO_3,\frac{1}{2}H_2O$, of which it appears to be a variety, This is probably also true of a substance called podolite,[70] mentioned among the new minerals in the annual report for 1907.

Datolite.—Good crystals of this mineral occur at the junction of a serpentine with a hornblende-schist at Park Bean Cove, Mullion, Cornwall.[71] The analytical results agree very closely with those

[64] W. E. Ford, *Amer. J. Sci.*, 1910, [iv], **30**, 24.

[65] G. P. Tschernik, *Bull. Acad. Sci. St. Pétersbourg*, 1909, [vi], **3**, 1203 ; *A.*, ii, 136.

[66] T. Crook and G. S. Blake, *Min. Mag.*, 1910, **15**, 271 ; *A.*, ii, 308.

[67] L. Duparc, R. Sabot, and M. Wunder, *Arch. Sci. phys. nat.*, 1910, [iv], **29**, 62 ; *A.*, ii, 221.

[68] C. Palache, *Amer. J. Sci.*, 1910, [iv], **29**, 185 ; *A.*, ii, 219.

[69] A. Lacroix, *Compt. rend.*, 1910, **150**, 1388 ; *A.*, ii, 622.

[70] W. T. Schaller, *Amer. J. Sci.*, 1910, [iv], **30**, 309 ; *A.*, ii, 1076.

[71] W. F. P. McLintock, *Min. Mag.*, 1910, **15**, 407 ; *A.*, ii, 782

required by the usual formula, $HCaBSiO_5$. The sp. gr. is 3·001, and the optical constants as follows: $\alpha=1·626$, $\beta=1·653$, $\gamma=1·670$. $2V_a=76°16'$ (sodium light). The optic axial plane is 010, and the acute bisectrix almost perpendicular to 100.

Dawsonite.—Crystals of this very rare mineral have been found to have the composition $Na_2O,Al_2O_3,2CO_2,2H_2O$.[72] They belong to the orthorhombic system, $a:b:c=0·6475:1:0·5339$.

Epidote.—A number of minerals collected by the Duke of the Abruzzi's expedition to Ruwenzori have been described by L. Colomba,[73] and analyses made of some, including three specimens of epidote. For two of these, the ratio $SiO_2:R_2O_3:(RO,R_2O)$ is 2 : 1 : 2; in the third, 10 : 5 : 9.

Euxenite.—Specimens from Eitland and from Arendal proved on analysis to be typical euxenites.[74] A third from Saetersdal must be classed as polycrase, whilst a specimen from South Carolina was found to contain more tantalic acid and less titanium than is usually present. Zirconium could not be detected in any of the samples. An analysis of a euxenite from Cooglegong, Western Australia, has also been published.[75]

Fahlerz.—An important contribution to our knowledge of this mineral has been made by A. Kretschmer,[76] who has not only recalculated the atomic ratios of 162 published analyses, but has himself examined specimens from fifteen different localities. The carefully selected material was decomposed by bromine, which was found preferable to chlorine, and the analyses were carried out with all precautions. The results are tabulated in the following form, which summarises the data obtained for a specimen from Horhausen: $(Cu_{2·47},Zn_{0·51})_{2·98}SbS_{3·19}$. His determinations lead him to the conclusion that the ratio $Cu+Zn:Sb$ is constant and equal to three, whereas the ratio $Cu:Zn$ is variable. He finds that an empirical formula of the type $(M'x,M''y)_3M'''S_{3+y/2}$ expresses the experimental results, when $M'=Cu$ and Ag, $M''=$ Zn,Fe,Pb,Hg,Mn,Ni, and $M'''=$ Sb,As,Bi. As regards the further interpretation of the results, Kretschmer points out that the formula of Prior and Spencer, $3R'_2S·R'''_2S_3+x6R''S·R'''_2S_3$, is in harmony with his own determinations, but as it involves the assumption of isomorphism between compounds of the type $Cu_6Sb_2S_6$ and of the type $Zn_6Sb_2S_9$, the part played by Cu_6S_3 in the one being taken by Zn_6S_6 in the other, he prefers to consider fahlerz as an isomorphous mixture of a zinc compound, $Zn_6Sb_2S_9$, with a copper compound,

72 R. P. D. Graham, *Trans. Roy. Soc. Canada*, 1908, [iii], **2**, iv, 165; *A.*, ii, 136.
73 "*Il Ruwenzori,*" *by the Duca degli Abruzzi, Milano*, 1909, **2**, 281; *A.*, ii, 967.
74 O. Hauser and F. Wirth, *Ber.*, 1909, **42**, 4443; *A.*, ii, 47.
75 E. S. Simpson, *Austral. Assoc. Report*, 1909, 310; *A.*, ii, 1077.
76 *Zeitsch. Kryst. Min.*, 1910, **48**, 484.

$Cu_9Sb_3S_9$, the two equivalent atomic groups being Zn_6Sb_2 and Cu_9Sb_3. The composition of fahlerz can then be satisfactorily represented as $xCu_9Sb_3S_9 + Zn_6Sb_2S_9$. The value of x varies from 2 to 10, and is most frequently 3 to 4.

Felspar Group.—Many members of this group have been examined during the past year, and we may direct attention to the series of analyses of French felspars published by Barbier and Gonnard.[77] Interest also attaches to the large aggregates which occur in the basalt of the Crookdene dyke, Northumberland, which have proved to be anorthite,[78] and in particular to the labradorite from the Altai Mountains in Mexico.[79] The latter material is particularly well suited for chemical and optical investigation, and is found in perfectly clear and almost colourless water-worn pebbles. It has been shown by Ford and Bradley to consist of albite and anorthite in the ratio 1 : 1·918. The sp. gr. is 2·718, the angle between the cleavages 85°49′, the angle of extinction on 010 is −24°37′, and on 001 is −12°13′.

Friedelite.—There is considerable uncertainty as to the formula which best expresses the composition of this rather rare mineral. The formula commonly adopted, $H_7(MnCl)Mn_4Si_4O_{16}$, demands less manganese and more chlorine than are commonly present. Palache[80] has found that $H_9(MnCl)Mn_7Si_6O_{24}$ represents fairly satisfactorily the composition of a specimen from Franklin Furnace, though more water was observed than this formula requires. The mineral has also been discovered in some quantity associated with rhodocrosite at Veitsch, in Styria.[81] Two analyses have been interpreted by Hofmann and Slavík as leading to the formulæ $(H,Cl)_8R_7Si_5O_{21}$ and $(H,Cl)_8R_8Si_5O_{22}$ respectively, where R is chiefly Mn with small quantities of Ca and Mg. The chlorine content of this material is considerably below the average, and it may possibly have undergone alteration.

Fergusonite.—The composition of a specimen from Cooglegong, Western Australia, agrees with the usually accepted formula, R_2O_3,Ta_2O_5.[82]

Garnet Group.—A number of members of this family have been analysed during the year. Worthy of note are the analyses of red garnets from diamond pipes in Rhodesia published by F. P. Mennell,[83] and the data for a spessartite from Madagascar given

[77] *Bull. Soc. franç. Min.*, 1910, **33**, 81; *A.*, ii, 419.

[78] M. K. Heslop and J. A. Smythe, *Quart. Journ. Geol. Soc.*, 1910, **66**, 1; *A.*, ii, 313.

[79] *Amer. J. Sci.*, 1910, [iv], **30**, 151; *A.*, ii, 874.

[80] *Ibid.*, **29**, 183; *A.*, ii, 220.

[81] *Bull. Intern. Acad. Sci. Bohême*, 1909; *A.*, ii, 314.

[82] E. S. Simpson, *Austral. Assoc. Report*, 1909, 310; *A.*, ii, 1077.

[83] *Quart. J. Geol. Soc.*, 1910, **66**, 353; *A.*, ii, 1078.

by L. Duparc [84] and his assistants. This mineral is of gem quality. Its composition is well expressed by the formula $Mn_3Al_2(SiO_4)_3$, small quantities of ferric oxide and of lime being present. The index of refraction is 1·7998 (sodium light). Sp. gr. 4·0586. A calcium iron garnet from Praborna, St. Marcel,[85] containing 7·81 per cent. of chromium oxide, has been examined by L. Colomba, who assigns it to the variety uvarovite.

Glauconite.—Submarine deposits containing glauconite, digested first with hydrochloric acid and then with sodium hydroxide, yield, on shaking with boiling water, a colloidal suspension of disintegrated glauconite, from which, on addition of a trace of acid, a green, flocculent precipitate separates. The precipitate separated by this process from material dredged off Panama and from the Agulhas Bank agrees fairly well with the formula $KFeSi_2O_6,H_2O$.[86] Microscopic study of glauconite grains suggests that the silicate is colloidal, and enclosed in a network of organic matter, the birefringence and pleochroism being probably the result of strain. Grass-green, flocculent particles, resembling glauconite, have been obtained by heating under pressure to 180° the clear, greenish-blue jelly which results when potassium silicate and potassio-ferric tartrate are mixed.

Grahamite.—The relations existing between the various types of asphalts and bitumens have been discussed by C. Richardson,[87] who suggests that the term grahamite should be confined to native bitumen characterised by a schistose or hackly fracture, sparing solubility in naphtha, and by a high percentage of residual coke. He has tabulated the occurrences of grahamites in America, and draws attention to the presence of vanadium in the ash of these substances.

Hambergite.—This rare mineral has been found in Madagascar.[88] Analysis of crystalline material leads to the formula $4GlO,B_2O_3,H_2O$.

Hetoerolite.—A black mineral, supposed to be a zinc hausmannite, was described under this name in 1877. This view of its nature has now been confirmed by analysis of a specimen from Franklin Furnace, New Jersey, which establishes the formula as ZnO,Mn_2O_3.[89] It crystallises in the tetragonal system.

Hulsite.—When first described, this mineral was believed to contain 25·27 per cent. of B_2O_3, and to have the composition

[84] *Arch. Sci. phys. nat.*, 1910, [iv], **29**, 62 ; *A.*, ii, 221.
[85] *Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 146 ; *A.*, ii, 968.
[86] W. A. Caspari, *Proc. Roy. Soc. Edin.*, 1910, **30**, 364 ; *A.*, ii, 722.
[87] *J. Amer. Chem. Soc.*, 1910, **32**, 1032 ; *A.*, ii, 964.
[88] A. Lacroix, *Bull. Soc. franç. Min.*, 1910, **33**, 49 ; *A.*, ii, 307.
[89] C. Palache, *Amer. J. Sci.*, 1910, [iv], **29**, 180 ; *A.*, ii, 219.

$7(Fe,Mg)O,Fe_2O_3,H_2O,4B_2O_3$.[90] A re-determination of the boron gives a much lower result, and it has been found that the mineral contains considerable quantities of tin overlooked in the first analysis.[91] The formula now regarded as most probable is $12(Fe,Mg)O,2Fe_2O_3,SnO_2,3B_2O_3,2H_2O$.

Humboldtine.—Crystals of this rare mineral have been observed in a vein containing iron and manganese at Cape d'Arco, Elba, and have been fully described under the name oxalite by E. Manasse.[92] It occurs in minute, orthorhombic prisms associated with the basal pinakoid. The composition is $FeC_2O_4,2H_2O$, a simpler formula than has hitherto been assigned to the mineral. The crystals are amber-yellow in colour, pleochroic, and strongly birefringent. The indices of refraction by the immersion method are $\beta = 1{\cdot}561$, $\gamma = 1{\cdot}692$; α could not be determined, but is less than 1·494. It seems likely that the mineral has resulted from the interaction of oxalic acid, or of an alkaline oxalate of organic origin with ferrous sulphate produced by the oxidation of marcasite.

Hydrogiobertite.—Analysis of the spherulitic material which occurs in some abundance in the Chiles Valley, Napa County, California, agrees with the formula $2MgO,CO_2,3H_2O$.[93]

Ixiolite.—To this species has been assigned a mineral from Wodgina, Western Australia, of the formula $3MnO,3Ta_2O_5,SnO_2$.[94]

Jarosite Group.—At Saint-Félix-de-Pallières, Gard, France, a mineral occurs in ochre-yellow, compact masses, consisting of minute crystals. It owes its origin to the action of the products of the oxidation of iron-pyrites on the gangue, and was described under the name pastreite in 1866. A new analysis[95] has revealed the presence of alkalis, and shows that the substance is jarosite, $K_2Fe_6(OH)_{12}(SO_4)_4$.

Plumbojarosite has been reported from American Fork, Utah. The minute, rhombohedral crystals have much the same composition as the material from New Mexico described by Penfield, and can be represented by the same formula, $PbFe_6(OH)_{12}(SO_4)_4$.[96] The crystals are brownish-red in colour, and exhibit the base and the fundamental rhombohedron. The refractive indices are high, ϵ being about 1·785, and $\omega > 1{\cdot}825$.

Kaolinite.—Much attention has been devoted of late to the study of clays, kaolin, and laterites, and a noteworthy contribution to our

[90] See *Ann. Report*, 1909, 224. [91] W. T. Schaller, *ibid.*, 543; *A.*, ii, 621.
[92] *Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 138; *A.*, ii, 967.
[93] R. C. Wells, *Amer. J. Sci.*, 1910, [iv], **30**, 189; *A.*, ii, 965.
[94] E. S. Simpson, *Austral. Assoc. Report*, 1909, 310; *A.*, ii, 1077.
[95] Azéma, *Bull. Soc. franç. Min.*, 1910, **33**, 130; *A.*, ii, 720.
[96] W. F. Hillebrand and F. E. Wright, *Amer. J. Sci.*, 1910, [iv], **30**, 191; *A.*, ii, 966.

knowledge of these substances has been made by J. M. van Bemmelen.[97] Clay, the product of the weathering of silicate rocks, consists, he thinks, of a mixture of crystalline particles of unaltered silicates with a colloidal substance, the result of chemical alteration. The latter contains a silicate resembling kaolin, having from 2 to 2·7 molecules of silica to 1 molecule of alumina, together with a fusible silicate whose composition ranges from 2·9 to 6 molecules of silica to 1 of alumina in the case of heavy clays, and within somewhat narrower limits in the case of light clays. Volcanic clays are rich in the fusible silicate, older clays containing increasing quantities of the other. Kaolinite and zeolites appear to be due to the prolonged action on clay of high temperatures or hot water. Laterite is found in association with both acid and basic rocks in temperate climates as well as in the tropics, and in some cases both lateritic and ordinary weathering proceed simultaneously. The result of lateritic alteration is a product in which the silica ratio falls below 3 : 1, and in which aluminium hydroxide is present. Pneumatolytic weathering gives rise to kaolinite, $Al_2O_3,2SiO_2,2H_2O$. Since apatite and muscovite are readily decomposed by pneumatolytic agencies, but are very resistant to ordinary weathering, their presence or absence enables us to distinguish between kaolinite and the products of ordinary weathering. In this connexion, we may note that a method of distinguishing between kaolin and allophane has been based on the behaviour of these substances towards dilute acetic acid.[98] A kaolin, in which the ratio $Al_2O_3 : SiO_2$ was 1 : 2, was shaken for eight days with 6 or 12 per cent. acetic acid. Only from 1 to $1\frac{1}{2}$ per cent. dissolved, and in the solution equal molecular proportions of alumina and silica were found. Allophane treated similarly was much more freely attacked, some 11 per cent. being dissolved. The ratio of alumina to silica in the dissolved part was the same as in the mineral itself. Laterites have been the subject of investigation by H. Arsandaux,[99] who, from analysis of a number of samples, has arrived at the conclusion that laterites are normal muscovites in which water of constitution has progressively replaced the alkalis. The silicates are gradually replaced by hydrated oxides of iron and aluminium, as the result of secondary change.

Kryptotile is an alteration product of prismatine, with which it occurs at Waldheim in Saxony.[1] Its composition agrees with the simple formula $HAlSiO_4$, but its mode of occurrence and properties suggest that it is to be regarded as a member of the mica family in

[97] *Zeitsch. anorg. Chem.*, 1910, **66**, 322 ; *A.*, ii, 419.
[98] R. van der Leeden, *Centr. Min.*, 1910, 289 ; *A.*, ii, 621.
[99] *Compt. rend.*, 1910, **150**, 1698 ; *A.*, ii, 723.
[1] J. Uhlig, *Zeitsch. Kryst. Min.*, 1910, **47**, 215 ; *A.*, ii, 311.

which alkalis are absent, and the formula is therefore to be written $H_3Al_3Si_3O_{12}$.

Langbeinite occurs embedded in rock-salt at Hall, Tyrol.[2] It forms nodules, which, if exposed to the atmosphere, soon become coated with picromerite, $K_2SO_4,MgSO_4,6H_2O$, and epsomite. The composition of the material is $K_2SO_4,2MgSO_4$. Refractive index, 1·5347 (sodium light). Sp. gr. 2·825.

Lansfordite.—The water from the mineral springs at Rohitsch, Styria, when evaporated at 2°, deposits large monoclinic crystals of $MgCO_3,5H_2O$.[3] This substance is not formed above 6°, and begins to lose water at 20°. A comparison of these crystals with those of lansfordite, hitherto believed to be an anorthic mineral of the formula $3MgCO_3,Mg(OH)_2,21H_2O$, leads to the conclusion that they are identical. The crystallographic constants are as follows: $a : b : c = 1·6079 : 1 : 0·9524$, $\beta = 78°36'$. These conclusions have received confirmation from another quarter,[4] for it has been found that when the mixture of calcium and magnesium oxides obtained by calcining dolomite is suspended in water and treated at 10° with carbon dioxide under a pressure of from 5 to 6 atmospheres, only MgO is dissolved, and the filtrate deposits monoclinic crystals, $a : b : c = 1·6323 : 1 : 0·96676$, $\beta = 77°51'$, which have the composition $MgCO_3,5H_2O$, and appear to be identical in form with lansfordite.

Lanthanite.—Material from Bastnäs, Sweden, has been found to contain 28·34 per cent. $(La,Di)_2O_3$, and 25·52 per cent. of cerium oxide.[5] Like the American lanthanite, its composition may be expressed by the general formula $R_2O_3,3CO_2,8H_2O$.

Ludgwigite has recently been observed in Montana,[6] having only been known previously from Hungary. The formula $3MgO,FeO,Fe_2O_3,B_2O_3$, assigned to the Hungarian mineral, has been confirmed by a new analysis, and the American specimen shown to conform to the same type, part of the magnesia being, however, isomorphously replaced by ferrous oxide. The mineral occurs in small, dark green or nearly black spherulites in a metamorphic limestone containing large bodies of magnetite.

Manganosite.—This rare species has hitherto only been found in Sweden, but recently it has been observed as irregular, dark green grains, exhibiting cubic cleavage, associated with franklinite and zincite at Franklin Furnace.[7] Its formula is MnO, small quantities of zinc being also present.

[2] R. Görgey, *Tsch. Min. Mitt.*, 1909, **28**, 334 ; *A.*, ii, 309.
[3] H. Leitmeier, *Zeitsch. Kryst. Min.*, 1909, **47**, 104 ; *A.*, ii, 49.
[4] G. Cesàro, *Bull. Acad. roy. Belg.*, 1910, 234 ; *A.*, ii, 613.
[5] G. Lindström, *Geol. För. Förh. Stockholm*, 1910, **32**, 206 ; *A.*, ii, 965.
[6] W. T. Schaller, *Amer. J. Sci.*, 1910, [iv], **30**, 146 ; *A.*, ii, 873.
[7] C. Palache, *ibid.*, **29**, 178 ; *A.*, ii, 219.

Mica Group.—The analyses which have been published of members of this group call for no special remark, but we may note that the green mica crystals which occur in the dolomite of the Binnenthal have been shown by Prior[8] to belong to the variety termed fuchsite.

Microlite.—This mineral is essentially a calcium pyrotantalate. A specimen from Wodgina, Western Australia, has been analysed by E. S. Simpson.[9]

Minervite.—A soft, white, powdery substance, apparently homogeneous, from the Island of Réunion, has been found to have the composition $2AlPO_4,(K,NH_4,H)_3PO_4,7\frac{1}{2}H_2O$. It appears to be similar to minervite and palmerite.[10]

Nepheline.—The so-called pseudonepheline or pseudosommite, from Capo di Bove, resembles nepheline in its crystallographic characters, but has somewhat different optical properties. The formula is $(Na,K)AlSiO_4$, corresponding with a lower percentage of silica than is found in nepheline.[11]

Nesquehonite.—The waters of the mineral springs at Rohitsch, Styria, contain carbon dioxide, with considerable quantities of magnesium carbonate, sodium carbonate, and sodium sulphate.[12] On evaporation at temperatures of 13° or 20°, these waters deposit orthorhombic needles of nesquehonite, $MgCO_3,3H_2O$, followed after some days by indistinct crystals of aragonite, a mineral found in fine groups at the spring (see also lansfordite).

Paigeite.—This mineral occurs associated with hulsite and magnetite in the neighbourhood of Brooks Mountain, Seward Peninsula.[13] As is also true of hulsite, it has been found that the formula first assigned to the mineral needs revision, the amount of boron having been at first considerably over-estimated, and the tin altogether overlooked. The formula now suggested for paigeite is $30FeO,5Fe_2O_3,SnO_2,6B_2O_3,5H_2O$, although the possibility that the substance may be a borate of iron mixed with hulsite has to be borne in mind.

Patronite.—In the course of a description of the vanadium deposits in Peru, D. F. Hewett[14] gives analyses of specimens of patronite purer than that examined by Hillebrand, and suggests the formula $V_2S_5 + nS$. Secondary vanadium compounds are formed

[8] *Min. Mag.*, 1910, **15**, 385; *A.*, ii, 781.

[9] *Austral. Assoc. Report*, 1909, 310; *A.*, ii, 1077.

[10] A. Lacroix, *Bull. Soc. franç. Min.*, 1910, **33**, 34; *A.*, ii, 308.

[11] F. Zambonini, *Rend. Accad. Sci. Fis. Mat. Napoli*, 1910, [iiia], **16**, 83; *A.*, ii, 1078.

[12] H. Leitmeier, *Zeitsch. Kryst. Min.*, 1909, **47**, 104; *A.*, ii, 49.

[13] W. T. Schaller, *Amer. J. Sci.*, 1910, [iv], **29**, 543; *A.*, ii, 621.

[14] *Trans. Amer. Inst. Mining Engineers*, 1910, **40** (1909), 274; *A.*, ii, 719.

by the oxidation of these ores, and preliminary descriptions are given of these, some of which may prove to be new species.

Pilolite.—Thin, flexible sheets of "mountain leather," from various localities in the west of the Province of Süchwan, China, consists of interlaced fibres, showing straight extinction.[15] The composition corresponds with the formula $Al_2Si_2O_7,2MgSi_2O_5,7H_2O$, and the mineral is therefore not a variety of asbestiform serpentine or amphibole.

Plumboniobite was mentioned among the new minerals last year. The following formula is now proposed for it[16]:

$$R''_2Cb_2O_7,R'''_4(Cb_2O_7)_3,$$

where R'' represents Pb, Fe, UO, and Ca, and R''' represents Y, Gd, Sm, and Al.

Prismatine.—This mineral occurs in granulite at Waldheim, in Saxony, and was described by A. Sauer in 1886. Its identity with kornerupine was suggested by Ussing in 1889. It has lately been the subject of a careful reinvestigation,[17] which, whilst confirming in the main the work of previous observers, has resulted in the determination of the axial ratios of the orthorhombic crystals, and in a more accurate knowledge of the chemical composition. This appears to be best expressed as $NaH_3Mg_6Al_{12}Si_7O_{40}$, some of the magnesia being replaced by ferrous oxide, and some of the alumina by ferric iron. The composition of kornerupine may be represented by the analogous formula $H_2Mg_7Al_{12}Si_7O_{40}$; the two minerals may therefore be regarded as distinct but isomorphous species.

Pucherite.—A specimen of this rare vanadate of bismuth has been found in chrome-yellow, crystalline grains in the concentrates from an oxidised quartz reef at Niagara, Western Australia.[18] The composition is represented by the formula $BiVO_4$.

Pyroxene Group.—Analyses of the varieties termed jeffersonite and schefferite have been published by C. Palache.[19] The composition of a green chrome-diopside from a diamond pipe in Rhodesia has been recorded by F. P. Mennell,[20] and a number of analyses of augite from the basalt of the Rhön Mountains have been made by X. Galkin.[21] The last are all very similar in composition, and the results obtained have been fully discussed in the light of the work of Penfield and Tschermak, although no very definite conclusions have been drawn.

[15] G. S. Whitby, *Min. Mag.*, 1910, **15**, 294; *A.*, ii, 313.
[16] O. Hauser, *Ber.*, 1910, **43**, 417; *A.*, ii, 221.
[17] J. Uhlig, *Zeitsch. Kryst. Min.*, 1910, **47**, 215; *A.*, ii, 311.
[18] E. Griffiths, *J. Roy. Soc. New South Wales*, 1908, **42**, 251; *A.*, ii, 47.
[19] *Amer. J. Sci.*, 1910, [iv], **29**, 180; *A.*, ii, 219.
[20] *Quart. J. Geol. Soc.*, 1910, **66**, 353; *A.*, ii, 1078.
[21] *Jahrb. Min. Beil.-Bd.*, 1910, **29**, 681; *A.*, ii, 721.

Rhabdite is a phosphide of iron and nickel found in minute, tetragonal prisms in certain meteoric irons, and a phosphide of iron formed by combustion in the coal mines of Commentry, France, has been referred to the same species. The latter substance has lately been subjected to metallographic examination and chemical analysis,[22] with the result that it has been shown to be a mixture of iron and a phosphide, Fe_3P, together with small quantities of FeS.

Rhodonite.—Well-crystallised material from the Radauthal, Harz, has a composition agreeing with the general formula $R''SiO_3$,[23] where R'' is Mn and Ca (CaO = 14·18 per cent.).

Rivotite.—At Trazein, near Sentein, France, an ore containing copper, silver, and antimony is being worked in dolomites of Devonian age.[24] On microscopical examination, it was seen to consist of grains of tetrahedrite surrounded by concentric layers of a golden-yellow, isotropic material, which proved to be stibiconite, Sb_2O_4,H_2O, together with layers of a greenish-yellow, birefringent substance. The latter was soluble in ammonia and in acetic acid, and is malachite. A mineral termed rivotite, originally described from Spain, has similar characters, and is therefore to be regarded as a mixture of malachite and stibiconite resulting from the alteration of tetrahedrite.

Sapphire.—A. Verneuil[25] has found that this gem can be made artificially by fusing in the oxyhydrogen flame alumina containing 1·5 per cent. of magnetite and 0·5 per cent. of titanic acid. The physical properties of these stones agree closely with those of the natural mineral, and on analysis traces of Fe_2O_3 and from 0·11 to 0·13 per cent. of TiO_2 were found.[26]

Scapolite Group.—A specimen of mizzonite from Cape d'Arco, Elba, has been found to consist of three molecules of marialite, $Na_4[AlCl]Al_2[Si_3O_8]_3$, and two molecules of meionite, $Ca_4[AlO]Al_2[Si_2AlO_8]_3$, and to possess the corresponding physical properties.[27]

The views as to the constitution of the scapolite group, originally propounded by Tschermak, have, moreover, been abundantly confirmed by Himmelbauer,[28] who, in a valuable and elaborate memoir, has tabulated the results of previous observers, and has recorded the observations he himself has made on a number of members of this family. He has measured with great care the densities and

[22] Oswald, *Bull. Soc. franç. Min.*, 1910, **33**, 88.
[23] J. Fromme, *Tsch. Min. Mitt.*, 1909, **28**, 308; *A.*, ii, 314.
[24] A. Lacroix, *Bull. Soc. franç. Min.*, 1910, **33**, 190; *A.*, ii, 782.
[25] *Compt. rend.*, 1910, **150**, 185; *A.*, ii, 212.
[26] A. J. Moses, *Amer. J. Sci.*, 1910, [iv], **30**, 271; *A.*, ii, 965.
[27] E. Manasse, *Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 211; *A.*, ii, 967.
[28] *Sitzungsber. K. Akad. Wiss. Wien.*, 1910, **119** i, 115.

the crystallographic and optical constants of specimens from various localities, and has determined their melting points by the methods elaborated by Doelter. Further, he has examined, by Tschermak's method, the nature of the silicic acids, from which these substances are derived, and has by analysis estimated the proportions in which the two constituents, meionite and marialite, enter into their composition. He concludes that from the crystallographic, physical, and chemical aspect, the scapolites exhibit the criteria of an isomorphous series. Within the limits of experimental error, their properties are continuous functions of their composition. The fact that these limits are tolerably wide is due to the impurity of the material investigated.

Seligmannite.—From a consideration of its crystalline form, it was considered probable that this rare mineral from the Binnenthal would prove to be a sulpharsenite of copper and lead, $CuPbAsS_3$, isomorphous with bournonite, $CuPbSbS_3$. This prediction has now been fully confirmed by an analysis made by G. T. Prior.[29]

Ullmannite.—An interesting occurrence of this mineral has been reported from the New Brancepeth Colliery, near Durham.[30]. The crystals are of cubic or octahedral habit, and often form parallel growths with the galena with which they are associated. The composition is NiSbS.

Vanthoffite.—This mineral occurs as nodules embedded in blödite, (Na_2SO_4,$MgSO_4$,$4H_2O$), and associated with löweite,

$$(2Na_2SO_4,2MgSO_4,5H_2O),$$

at Hall, Tyrol. The composition agrees very closely with the formula $3Na_2SO_4$,$MgSO_4$.[31] The crystal system is doubtful, but the mineral is birefringent, and the following values were obtained for the refractive indices by the immersion method in sodium light: $\alpha = 1{\cdot}4855$, $\beta = 1{\cdot}4876$, $\gamma = 1{\cdot}4893$. Sp. gr. $= 2{\cdot}694$.

Variscite.—The formula Al_2O_3,P_2O_5,$5H_2O$ has been assigned to a pale apple-green substance incrusting black shale in an iron mine at Vashegy, Hungary.[32] The mineral contains one molecule more water than is usually present in variscite.

Vesuvianite.—Bluish-green, fibrous material from Franklin Furnace agrees closely in composition with cyprine from Tellemarken, Norway, although the latter contains less water and more fluorine.[33] The formula is $H_8(Al,Fe)_6Ca_{12}Si_{10}O_{45}$.

Willemite.—The axial ratio and refractive indices of colourless or pale green crystals from Franklin Furnace have been found to

[29] *Min. Mag.*, 1910, **15**, 385; *A.*, ii, 781.
[30] L. J. Spencer, *ibid.*, 302; *A.*, ii, 307.
[31] R. Görgey, *Tsch. Min. Mitt.*, 1909, **28**, 334; *A.*, ii, 309.
[32] K. Zimányi, *Ber. aus Ungarn*, 1909, **25**, 241; *A.*, ii, 307.
[33] C. Palache, *Amer. J. Sci.*, 1910, [iv], **29**, 184; *A.*, ii, 219

be as follows[34]: $a : c = 1 : 0·6612$, $\omega = 1·6939$, $\epsilon = 1·7230$ (sodium light).

Wolframite.—The mixture of rare earths obtained from the Zinnwald wolframite contains about 56 per cent. of scandium oxide, which appears to be present to the extent of about 0·1 per cent. in the original mineral. A similar proportion has been detected in wolframite from Sadisdorf, near Schmiedeberg.[35] The presence of scandium in wolframite from Sadisdorf has been confirmed by Eberhard,[36] who has also detected it spectroscopically in a number of minerals and rocks, more particularly in æschynite and cassiterite from Swaziland, in monazite and wiikite from Finland, and in cassiterite from Japan. It appears to be almost constantly present in the minerals and rocks associated with tin-ores.

Zeolite Group.—Among the recent investigations of members of this group we may notice, in the first place, the careful study of the acicular crystals of *mesolite* from the Faroe Islands, for which we are indebted to R. Görgey.[37] The crystals are apparently monoclinic, but optical examination shows that they are really triclinic and twinned. In composition they correspond with a mixture of one molecule of natrolite, $Na_2Al_2Si_3O_{10},2H_2O$, with two molecules of scolecite, $CaAl_2Si_3O_{10},3H_2O$. As both these minerals are, however, monoclinic, the conclusion is arrived at that mesolite is to be regarded as a double salt, rather than as an isomorphous mixture. The optical properties of mesolite and allied substances have also been examined in detail by G. Cesàro.[38] The large twinned crystals of *phillipsite*, which occur in basalt at Sirgwitz in Silesia, contain an unusually high percentage of magnesium oxide (4·53 per cent.).[39] Their composition may be represented as

$$15SiO_2,4Al_2O_3,5(Ca,Mg,K_2)O,20H_2O.$$

Magnesium oxide has also been reported by J. Fromme[40] in a mesolite from the Radauthal, Harz, and in an apophyllite from the same locality. The latter is also remarkable as containing alumina (1·78 per cent.), apparently as an essential constituent.

Here may be recorded some interesting experiments which have been made on the absorption of vapours by zeolites. It has long been known that certain zeolites, when dehydrated, will absorb not only water, but air and ammonia, and it has now been shown that vapours of iodine, bromine, mercury, calomel, cinnabar, and sulphur

[34] C. Palache, *Amer. J. Sci.*, 1910, [iv], **29**, 184 ; *A*, ii, 219.
[35] R. J. Meyer and H. Winter, *Zeitsch. anorg. Chem.*, 1910, **67**, 498 ; *A.*, ii, 853.
[36] *Sitzungsber. K. Akad. Wiss. Berlin*, 1910, 404 ; *A.*, ii, 509.
[37] *Tsch. Min. Mitt.*, 1909, **28**, 77 ; *A.*, ii, 312.
[38] *Bull. Acad. roy. Belg.*, 1909, 435.
[39] P. Barbier and F. Gonnard, *Bull. Soc. franç. Min.*, 1910, **33**, 79 ; *A.*, ii, 418.
[40] *Tsch. Min. Mitt.*, 1909, **28**, 305 ; *A.*, ii, 314.

may be taken up.[41] Chabazite, for example, may absorb as much as 27 per cent. of mercury. Marked changes in the optical properties accompany these phenomena. We may also draw attention to an investigation into the rate at which an artificial sodium zeolite is attacked by certain chloride solutions.[42] It is found that the velocity of the reaction is at first very great, but gradually diminishes. Rise of temperature increases the rate of change, and when solutions of the chlorides of magnesium, calcium, strontium, and barium are employed, increased velocity of attack accompanies increase in the atomic weight of the metallic iron.

Meteorites.

Laboratory work on the properties of nickel-iron alloys might fairly be expected to throw light on the nature of the meteoric irons, but although attempts in this direction have not been wanting, the conclusions so far arrived at appear to be somewhat contradictory. Last year reference was made to a paper by Fraenkel and Tammann, in which evidence was brought forward to prove that meteoric nickel-iron is unstable at low temperatures. That this is not the case is now maintained by Guertler,[43] who has attempted to show that the formation of the characteristic meteoric structure can only occur at low temperatures and with extreme slowness. In this connexion, we may note that, according to Ruer and Schüz,[44] the system iron-nickel gives a continuous freezing-point curve with a shallow minimum. From these experiments and from a series of determinations of the temperatures of magnetic transformation, they find indications of the existence of a compound $FeNi_2$.

Among recent investigations of individual meteorites, the following may be recorded.

Angra dos Reis.—This stone is remarkable as consisting mainly (92·89 per cent.) of an augite resembling in its optical characters the titaniferous augite of certain basaltic rocks. The other constituents are olivine, pyrrhotite, apatite in small grains, and glass particles. On looking for titanium, 2·39 per cent. of TiO_2 was found in the stone.[45] The analysis published in 1887, in which the presence of titanium was overlooked, therefore requires correction.

Chandakapur.—A thorough examination has been made of a portion of the specimen preserved in the Oxford University Museum.[46] The meteorite consists mainly of olivine (53·47 per cent.) and pyroxenes and felspars (33·89 per cent.), and bears a

[41] F. Grandjean, *Bull. Soc. franç. Min.*, 1910, **33**, 5; *A.*, ii, 311.

[42] A. G. Doroschewsky and A. Bardt, *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 435; *A.*, ii, 615.

[43] *Zeitsch. physikal. Chem.*, 1910, **74**, 428; *A.*, ii, 833.

[44] *Metallurgie*, 1910, **7**, 415; *A.*, ii, 959.

[45] E. Ludwig and G. Tschermak, *Tsch. Min. Mitt.*, 1909, **28**, 110; *A.*, ii, 315.

[46] H. L. Bowman and H. E. Clarke, *Min. Mag.*, 1910, **15**, 350; *A.*, ii, 783.

noticeable resemblance to the chondrites of Makariwa, Krähenberg, Waconda, and Nerft. The silicates are very rich in aluminium. The metallic alloy (5·8 per cent.) is rather poor in nickel. The other constituents are troilite, schreibersite, chromite, magnetite, and rust.

Coon Butte.—The origin of the great crater-like depression known as Coon Butte, in Arizona, has been the subject of much speculation. The presence in and around it of numerous masses of meteoric iron has suggested that it was produced by the impact of an immense meteorite or swarm of meteorites. This view was discussed by Merrill in 1908, and has met with considerable acceptance, although the alternative explanation of formation by volcanic action is still preferred by some. D. M. Barringer[47] finds support for the meteoric hypothesis in the results of a careful exploration of the crater, and has recorded his observations and conclusions in a beautifully illustrated memoir (privately printed), entitled "The Meteor Crater in Northern Central Arizona."

Goamus.—This meteorite takes its name from the farm called Goamus, near Gibeon, in German South-West Africa.[48] It is an iron, and remarkable for its octahedral structure, lamellæ parallel to cube faces being of subordinate importance.

Murnpeowie.—The discovery of an iron meteorite exceeding a ton in weight has been reported from Murnpeowie, South Australia.[49] Its fall was not observed, but there seems reason to believe that it took place in recent times. It is at present under investigation.

Shrewsbury.—A much-weathered mass was found in 1907 about seven miles north of Shrewsbury, York County, Pennsylvania.[50] On examination, it proved to be an octahedrite of medium coarseness, with broad bands of kamacite bordered by taenite. Troilite nodules and schreibersite are also present.

Simondium.—Two much-rusted masses, found about a foot below the surface in gravel at Simondium, Cape Colony, have been described by G. T. Prior.[51] They may be placed in the howardite group of Brezina's classification, and consist mainly of enstatite, olivine, and plagioclase felspar, together with magnetite, nodules of troilite, and particles of nickel-iron.

Thomson.—A small mass was found at Thomson, McDuffie County, Georgia, in 1888, but its existence has only recently been made public.[52] It appears to resemble the Möcs meteorite.

A. HUTCHINSON.

[47] *Smithsonian Misc. Contributions*, 1908, 461.
[48] F. Rinne, *Jahrb. Min.*, 1910, **1**, 115.
[49] L. Laybourne Smith, *Amer. J. Sci.*, 1910, [iv], **30**, 264.
[50] O. C. Farrington, *ibid.*, **29**, 350; *A.*, ii, 420.
[51] *Min. Mag.*, 1910, **15**, 312; *A.*, ii, 315.
[52] G. P. Merrill, *Amer. J. Sci.*, 1910, [iv], **29**, 368.

RADIOACTIVITY.

Standards and Units of Measurement.

AT the International Congress of Radiology at Brussels held during the year, after a general review of the question by Rutherford, an International Standards Committee was appointed and issued a Report.[1] As a member of this committee, Mme. Curie has consented to prepare a standard tube containing a known weight, approximately 20 milligrams, of radium (element) as chloride, which is to be kept in Paris, and is to serve as the primary international standard of radium. By suitable γ-ray methods of measurement, any required number of standards, having a known ratio to the primary, can then be prepared without elaborate chemical processes. The relatively somewhat large quantity chosen is necessary to secure a high degree of accuracy, the standard being primarily a standard mass of radium which, once prepared, will serve subsequently as a standard of γ-radiation, but for many purposes smaller sub-standards of about 1 milligram will be more generally useful. For measurement of smaller quantities of radium, such as are found in naturally occurring materials, the emanation generated by the radium is almost invariably employed. A new unit for the quantity of radium emanation was adopted, to be called the "curie," with the subdivisions millicurie, microcurie, etc., the curie being the mass of emanation in equilibrium with one gram of radium. Its mass is therefore λ_1/λ_2 gram, where λ_1 and λ_2 are the radioactive constants of radium and its emanation respectively. The unit frequently used, the amount of emanation generated per second by a gram of radium, is λ_2 curie, λ_2 being expressed in seconds. Recent determinations agree in making the value of $\lambda_2(\text{sec.})^{-1}$, $2{\cdot}08 \times 10^{-6}$ (p. 279).[2]

The absolute value of the ionisation current, in vessels of cylindrical form, given by known quantities of emanation has also been the subject of recent investigation.[3]

[1] *Le Radium*, 1910, **7**, *September Supplement*, p. 65.
[2] Mme. Curie, *Le Radium*, 1910, **7**, 32 ; *A.*, ii, 374.
[3] W. Duane and A. Laborde, *Compt. rend.*, 1910, **150**, 1421 ; *A.*, ii, 676.

The preparation of the primary standard will therefore bring about a great advance in reducing all radioactive measurements to a common standard, and in simplifying the expression of the results. Each laboratory now possesses its own provisional radium standard, as was the case in electrical laboratories with standards of resistance a few decades ago. The adoption of a common standard is of importance, not only for scientific, but also in technical, work where considerable uncertainty prevails.

α-Rays.

Counting Experiments.—Several important investigations have been published depending on the counting of α-particles by the scintillation method. In the first place, fresh information has in this way been obtained of the number of α-particles emitted in the successive changes of the thorium and actinium series.[4] Two parallel zinc sulphide screens, placed near together, formed two sides of a box into which emanation was allowed to diffuse from preparations of thorium or actinium. The number of scintillations from the active deposit and emanation together in equilibrium was in each case three times greater than that found for the active deposit alone, after the supply of emanation had been cut off and that initially present allowed to decay. Since in each case two sets of α-particles are furnished by the active deposit, four must be furnished by the emanation. By means of two similar microscopes, focussed on exactly opposite portions of the two screens, two observers counted the number of simultaneous scintillations. For the radium emanation and active deposit only a few per cent. of the scintillations occurred in pairs, but for the actinium emanation two-thirds of the total number of scintillations occurred as pairs simultaneously. For the thorium emanation a large number of rapidly succeeding scintillations were recorded, the interval varying from 0·5 second downward. Even with very few scintillations per minute, the appearance of a scintillation was usually the signal for that of another, which followed the first closely, after a distinct but very short interval. It appears therefore that the change of the thorium emanation is double, the product of the emanation having a period of average life of the order of one-fifth of a second. Interesting and suggestive as the experiments are, they are still far from complete, and many points remain unanswered, the method of investigation being extremely difficult and trying to the observer. The detection of the single scintillation, although possible, is very near the limit of visibility, especially in

[4] *Ann. Report,* 1909, 236 ; H. Geiger and E. Marsden, *Physikal. Zeitsch.*, 1910, **11**, 7 ; *A.*, ii, 92.

the case of the low-range α-particles of uranium. The obvious extension of the method just described to the problem whether the two α-particles from uranium are simultaneous or successive has not yet been accomplished. On the other hand, determinations have been made of the relative numbers of α-particles given by pure uranium and thorium compounds and by uranium and thorium minerals respectively, in which the complete disintegration series exist in equilibrium. These experiments have completely substantiated the view that uranium, alone in the uranium series, emits two α-particles per atom disintegrating, and, on this basis, bear out remarkably closely the number calculated from the fundamental constant [5] representing the number emitted per second ($3{\cdot}4 \times 10^{10}$) per gram of radium (free from products). Thus the calculated number, per second, per gram of uranium in equilibrium, is 96,700. The number found in one investigation [6] was 73,600, and in the other,[7] which was more complete, 96,000. In the latter research, the number found per gram of uranium in pure uranium oxide was 23,700, as compared with 11,600, the calculated number, if only one α-particle was expelled from each atom of uranium.

The distribution of the α-particles among the members of the thorium series, and the total number emitted per atom of thorium, are, as already pointed out, still incompletely known, but the total number given per second by one gram of thorium in equilibrium with its products was found to be 27,000. The period of uranium is known from the ratio of uranium and radium in minerals and the period of radium, but no such method for determining the period of thorium is possible. The datum just referred to will, however, enable the period of thorium to be calculated as soon as the total number of α-particles emitted per atom of thorium disintegrating is known. It has always been clear that the period of thorium must be many times greater than that of uranium.

An interesting result of the foregoing investigation was that the scintillations produced by the α-rays of ionium (range 2·8 cm.) were as bright or brighter than those from the α-rays of uranium, the range of which has previously been assumed, from indirect calculations, to be 3·5 cm. A preliminary direct estimate of the range of these particles by a scintillation method gave 2·7 cm., the lowest yet recorded. The low range of both α-particles from uranium is, on Rutherford's rule,[8] very strong, although not entirely conclusive, evidence that they cannot be derived from two successive changes, unless the second change is at least as slow as that of

[5] Called Q previously, *Ann. Report*, 1909, 234.
[6] J. N. Brown, *Proc. Roy. Soc.*, 1910, A, **84**, 151 ; *A.*, ii, 917.
[7] H. Geiger and E. Rutherford, *Phil. Mag.*, 1910, [vi], **20**, 691 ; *A.*, ii, 917.
[8] *Ann. Report*, 1907, 311.

ionium. But in this case uranium must be a chemically non-separable mixture of two elements differing in atomic weight by 4 units, in the constant proportion due to their genetic relationships (compare p. 285). The distribution of the α-particles from a polonium source with regard to time was found to be such as is to be expected from the theory of probability for a purely random distribution.[9]

The Sudden Disappearance of the α-Particle at the End of its Range.—Experiments [10] have shown that as the velocity of the α-particle diminishes in its passage through matter, there is a rapid increase in its liability to be scattered or turned from its initial direction by collision with an atom. The power of different atoms to scatter α-rays was found to be directly proportional to the atomic weight, and for gold to be inversely proportional to the cube of the velocity of the α-particle. A re-determination [11] of the diminution of velocity during passage through matter showed that the velocity of the α-particle at any point in its path is proportional to the cube root of the range it has still to run. At a point about 5 mm. from the end of the range, the number of α-particles in a stream, which previously has remained constant during the passage through matter, begins to diminish rapidly. This is not due to initial differences in the velocity of expulsion, for the most careful tests failed to show any such differences, but is brought about by differences in the individual chances of collision with the molecules of matter during the passage and by scattering. The ranges of Bragg are in reality the extreme ranges, the average ranges being some millimetres less. It is probable that the very rapid increase in the liability of the α-particle to be deflected and scattered on collision with an atom as its velocity diminishes accounts for the apparent suddenness with which the particle passes out of the range of detection. For the individual α-particle, the diminution of ionising power is not quite so sudden as is indicated by the Bragg curve, which is an average curve for a pencil of α-particles travelling, towards the end of the path, at slightly different speeds.

Fluorescence.—A quantitative examination of the fluorescence of zinc sulphide, willemite, and barium platinocyanide, exposed to α-rays, has shown that the reduction of luminosity with continued exposure, which is least rapid for willemite, and most rapid for barium platinocyanide, is accompanied by only a small reduction in the number of scintillations observed.[12] The theory is suggested that "active centres" exist in the fluorescent substance, which

[9] E. Rutherford and H. Geiger, *Phil. Mag.*, 1910, [vi], **20**, 698; *A.*, ii, 917.

[10] H. Geiger, *Proc. Roy. Soc.*, 1910, A, **83**, 492; *A.*, ii, 472.

[11] H. Geiger, *ibid.*, 505; *A.*, ii, 473; compare *Ann. Report*, 1906, 335.

[12] E. Marsden, *ibid.*, 548; *A.*, ii, 565; E. Rutherford, *ibid.*, 561; *A.*, ii, 565.

dissociate and give out light when struck by an α-particle, but, after having been once struck, become ineffective. At first each α-particle causes the dissociation of a number of these centres, but, as they become used up, fewer are available, causing the brightness, but not the number, of the individual scintillations to diminish. On this view it is calculated that the mean diameter of the active centres in zinc sulphide and willemite is not very much larger than the molecular diameter, which precludes the possibility that the scintillations are produced by the mechanical cleavage of small crystals. In barium platinocyanide the diameter of the active centres appears to be about a hundred times greater than in zinc sulphide. It has long been known that similar changes are produced in barium platinocyanide by grinding, and that simple re-crystallisation restores the salt to its initial condition.[13]

Pleochroic Halos.[14]—Just as the photographic plate reveals stars too faint to be visually detected, the pleochroic halo found in certain micaceous minerals, particularly biotite, zinnwaldite, and hornblende, integrates the α-ray effect of ages from tiny inclusions of radioactive material, themselves often barely visible in the centre of the halo. The diameter of a nucleus capable of evolving a fully developed halo is often less than 5×10^{-4} cm., and even if this were uraninite, the quantity of radium it contains is only 10^{-16} gram, and the number of α-particles given off is only about two per day. In certain embryonic halos, still quite unmistakable, the mass of matter in the nucleus is often sixteen times less, and as the material causing the halo is often zircon, not a very radioactive mineral, it follows that by this means quantities of radioactive matter can be recognised by mere inspection, which are many thousands of times less than can be detected in any other way. The production of the halo depends on the character of the surrounding matrix, and in one specimen of Leinster biotite, the halo was often found to be abruptly bisected where the darkened biotite abutted against completely limpid muscovite. In granites and syenites the halo is not continued into the quartz or felspar adjacent to the biotite or hornblende in which it develops. As the α-ray-sensitive mica is often associated in rocks with many common elements, without the occurrence of pleochroic halos, it may be concluded that α-radioactivity, at least, is certainly not a common property of matter too feeble to be directly detected.

A careful microscopic examination of these halos has revealed details of extraordinary interest. Owing to the ionisation of the α-ray increasing rapidly towards the end of its range to a maximum just before it ceases to ionise, the darkening in the halo is not

[13] *Ann. Report*, 1905, 301.

[14] J. Joly and A. L. Fletcher, *Phil. Mag.*, 1910, [vi], **19**, 630.

uniform, or uniformly varying from the centre to the edge, but there exist well-defined rings of greater intensity corresponding with the separate α-rays of different ranges. Taking into account the chemical composition and the density of the material and the known law of absorption of the α-rays, the various features of the halos correspond exactly with the known α-rays. No central "pupil" is ever found less in diameter than the range of the ionium α-ray, nor any "corona" greater than corresponds with the range of the α-ray from thorium-*C*. The uranium halos can be distinguished easily from the thorium halos, which are less frequently encountered, but both have been found side by side in the same specimen. In biotite, with nuclei of negligible size, the overall diameter of a good completely developed uranium halo is 0·033 mm., and of a thorium halo 0·040 mm. All stages of development have been observed in a single large crystal of biotite (variety, haughtonite) from Leinster granite. The phenomenon commences with the appearance of the embryonic halo, perfectly circular and usually structureless or with only a slightly darkened peripheral border, due to the slowest α-rays (ionium, radium, uranium). This does not start from the centre outward, but the earliest appearance is a very faint spherical darkening of the full diameter. These simple halos may be quite blackened up before the next stage, due to the α-rays of radium-*A* and -*C*, appears. The α-rays of radium-*F* and the emanation enlarge the diameter of this central "pupil" somewhat, at a later stage of development, without any clear annulus. The next stage seems to be the development of the "corona" due to radium-*C*, and it is only after this has commenced that the inner corona due to radium-*A* appears, which, quite inexplicably, seems always somewhat backward in its development. A beautiful series of microphotographs accompanies the paper, and in one, of a halo in biotite ($\times 450$ diameters), the central pupil, the outer corona due to radium-*C*, and the inner due to radium-*A* are shown with exquisite detail. In the last stage of the development, only the outer corona and central pupil, enlarged to somewhat more than the radius due to radium-*A*, can be separately distinguished, which enlargement may be due to actinium α-rays, but has not yet been fully explained. Fine capillary tubes of soda-glass, which have contained radium emanation, show in transverse section a coloured region extending about 0·04 mm., corresponding with the natural pleochroic halo.[15]

Helium.

Production of Helium by Radioactive Substances.—The identity of the α-particles expelled in the radium series with atoms of helium

[15] E. Rutherford, *Mem. Manchester Phil. Soc.*, 1909, **54**, [v], 1 ; *A.*, ii, 175.

has been completely established,[16] and it is therefore advisable to consider the researches on the connexion of helium with radioactivity immediately after those dealing with the α-rays. Two new determinations of the rate of production of helium from radium have been made. The first [17] refers to the experiment already described,[18] in which the rate of production previously given, 0·37 cu.mm. (per gram of radium per day), was erroneous, and should have been 0·499 cu.mm. Over a further period of nine months the rate of production was 0·463, and it is considered that the true value probably lies between these two limits. The theoretical value is 0·433 cu.mm. In the second determination,[19] 0·2 gram of radium chloride, freed by chemical treatment from polonium and radium-*D*, was allowed to accumulate helium for eighty-three days. The rate of production found corresponded with 0·447 cu.mm. (per gram per day). The production of helium from polonium, which is referred to incidentally in the work just described, has been established in the investigation on this substance,[20] described more fully later (p. 281). Part of a very active polonium preparation, derived from several tons of pitchblende, generated 1·3 cu.mm. of helium in one hundred days, as compared with the value 1·6 cu.mm., calculated from the number of α-particles expelled. An important determination of the rate of production of helium in the minerals thorianite and Joachimsthal pitchblende [21] has given the following results:

	U_3O_8.	ThO_2.	Rate found.	Rate calculated.
Thorianite	24 5	65·44	$3{\cdot}7 \times 10^{-8}$	$3{\cdot}42 \times 10^{-8}$
	13·1	72·65	$2{\cdot}79 \times 10^{-8}$	$2{\cdot}67 \times 10^{-8}$
Pitchblende	37·6	—	$3{\cdot}16 \times 10^{-8}$	$2{\cdot}95 \times 10^{-8}$

The table shows the percentage of uranium oxide and thoria in the minerals, and the rate of production of helium found in c.c. per gram of mineral per annum. The work was published prior to that already considered (p. 258) on the number of α-particles expelled per second per gram of uranium and thorium in minerals, but I have, from these numbers, calculated the theoretical rates of production of helium for the three minerals, and shown the result in the last column of the table. Considering the great difficulties of the experiments, there is a wonderful agreement between the values found and calculated.

Helium in Minerals.—The minimum ages of the two thorianites

[16] *Ann. Report*, 1909, 232.

[17] Sir J. Dewar, *Proc. Roy. Soc.*, 1910, A, **83**, 404 ; *A.*, ii, 376.

[18] *Ann Report*, 1909, 249.

[19] E. Rutherford and B. Boltwood, *Mem. Manchester Phil. Soc.*, 1909, **54**, [vi], 1 ; *A.*, ii, 175.

[20] Mme. Curie and A. Debierne, *Compt. rend.*, 1910, **150**, 386 ; *A.*, ii, 251.

[21] Hon. R. J. Strutt, *Proc. Roy. Soc.*, 1910, A, **84**, 379 ; *A.*, ii, 1023.

used in the last investigation, calculated from the rate of production of helium and the quantity of helium in the mineral, are respectively 250 and 280 million years. As certainly some of the helium escapes, the real ages must exceed this.[22] But several examples of the Archean rocks show a higher ratio of helium to thorium and uranium than thorianite,[23] a minimum age of 700 million years being indicated by this method for certain sphenes. Minerals like zircon and sphene contain hundreds of times as much helium as the average for the rocks in which they are constituents, so that the whole of the contained helium must have been generated since the consolidation of the rock and the separation of the mineral. The minimum ages for three other minerals found by these methods were, in millions of years, (1) sphærosiderite (oligocene), 8·4; (2) hæmatite (eocene), 31; (3) hæmatite (carboniferous limestone), 150. In explanation of the anomalous case of beryl, which contains helium out of all proportion to its radioactive constituents, it has been suggested that the helium is derived from radium or ionium initially deposited with the mineral, which, in the absence of its parent element, has completely disintegrated.

Distinct traces of helium have been found in many minerals, not appreciably radioactive, such as castorite and tourmaline, in addition to beryl, whilst the strongly radioactive minerals formed in the contemporaneous eruptions of Vesuvius, for example, cotunnite, the radioactivity of which is due to radium-*D* and its products without radium, do not contain helium. In the recent strongly radioactive minerals, carnotite and tobernite, helium in minute quantity has been detected, but in autunite the amount in certain specimens is not detectable.[24] Autunite is interesting, also, since it contains practically no lead, and because its radium-to-uranium ratio is abnormally low.[25]

An examination of the helium content and the radium-to-uranium ratio of several specimens of Portuguese autunite showed that both quantities vary very much in different specimens. In one specimen, specially chosen on account of its fresh and unaltered appearance, no helium was found, although the amount formed in only thirty years could have been detected, whilst the radium ratio was the highest of all those examined, being 70 per cent. of the equilibrium amount. In the other specimens helium was found, in one case in considerable amount, corresponding with 70,000 years' accumulation. As the helium increased, however, the radium ratio decreased to

22 *Ann. Report*, 1909, 250.

23 Hon. R. J. Strutt, *Proc. Roy. Soc.*, 1910, A, **83**, 298, and A, **84**, 194; *A.*, ii, 175, 920.

24 A. Piutti, *Le Radium*, 1910, **7**, 146, 178; *A.*, ii, 677, 767.

25 *Ann. Report*, 1909, 250, 260.

a minimum, and then again rose more slowly, suggesting, if the few specimens so far examined are representative, that the formation of Portuguese autunite is a process now in actual operation, and that the crystals when first deposited contain the radium, but not the ionium associated with the uranium in the parent mineral. The radium present, in consequence, decays for the first few thousand years after the formation of the crystals until a minimum is reached, when fresh begins to be supplied from regenerated ionium.[26] Private information, supplied by the owners of Portuguese autunite mines, makes it clear that most interesting geological processes are there in full operation at the present day. For the whole mass of material treated, the Rutherford-Boltwood ratio of radium to uranium is found to hold accurately. In selected crystals, however, an exceedingly low value for this ratio is often found, whilst the material of the rock walls in which the veins of autunite occur sometimes contain a relatively high content of radium and no chemically detectable quantity of uranium. The case is probably completely analogous to the superficial coating of the pyromorphite of Issy-l'Evêque with radium, which has been connected with the existence of an autunite deposit in the neighbourhood.[27] In both cases, however, it is probable that it is not the radium which is separated by the agency of percolating water, but its parent, ionium. A million years hence such rocks might well contain detectable quantities of helium and no radioactive matter.

The presence of helium to the extent of 0·17 volume per cent. in inflammable natural gas (83·6 per cent. hydrogen, 4·4 per cent. methane, 12 per cent. inert residue), issuing from the carnallite beds of Leopoldshall, has suggested that the origin of the gas may be due to the decomposition of water by radioactive impurities in the carnallite. The oxygen would go to oxidise the ferrous chloride present as rinnite ($FeCl_2,3KCl,NaCl$). The well-known blue rock salt found in these mines may be due to the action of the rays of the radioactive matter on the sodium chloride.[28]

β-Rays.

Homogeneous β-Radiation.—Foremost in the work on β-rays must be placed a notable advance, bearing out the working theory before alluded to,[29] that in any single disintegration only one type of β-radiation is expelled, which, like the α-radiation, is homogeneous

[26] F. Soddy, *Le Radium*, 1910, **7**, 295; *A.*, 1911, ii, 6.
[27] *Ann. Report*, 1909, 260.
[28] Ernst Erdmann, *Ber.*, 1910, **43**, 777; *A.*, ii, 376.
[29] *Ann. Report*, 1909, 241.

as regards initial velocity of expulsion, and is exponentially absorbed by matter. If a beam of β-rays, after passage through a slit, is deviated in a suitable magnetic field and allowed to fall on a photographic plate, the resultant image will be like a continuous spectrum, if the rays are perfectly heterogeneous, and like a line spectrum if they are composed of several types of distinct homogeneous bundles of rays. The β-rays from the active deposit of thorium gave a photograph having a single sharp line corresponding with the hard β-rays of thorium-*D*, and another corresponding with the soft β-rays of thorium-*A*, in addition to others due to very soft β-rays, so feebly penetrating that they cannot be differentiated from α-rays in ordinary absorption measurements. A radiothorium preparation showed, in addition, a previously unrecognised very soft β-radiation, due to thorium-*X*, which separate experiments showed was about three times as readily absorbed as the β-rays of thorium-*A*.[30] Radium-*E* gave one not very sharp line, whilst mesothorium-2 showed, apart from four lines due to extremely soft β-rays, only a broad band, indicating that its penetrating β-rays, like those of radium-*C*, are complex. It is perhaps natural that the most definite results in favour of distinct types of β-rays should first be obtained for an active deposit where no absorption takes place in the radioactive matter itself, for the heterogeneity of β-rays from a thick layer of substance is not inconsistent with an initial homogeneity subsequently modified by absorption in the material. Thus the β-rays from a thick layer of radium-*E* have been shown by magnetic deflexion experiments to be heterogeneous, and different bundles of rays can be sorted out of widely different penerating power, the absorption coefficient $[\mu(\text{cm.})^{-1}]$[31] varying between 13 and 62·5. Yet as a whole the radiation is exponentially absorbed $[\mu(\text{cm.})^{-1}=43]$.[32] This result supports the view that the exponential law of absorption is indicative of heterogeneity of the rays with a certain distribution of velocity among the constituents of the beam, rather than the older view that because the rays are exponentially absorbed therefore they are homogeneous.[33] At the same time a repetition of the experiments which led before to the conclusion that homogeneous β-rays, obtained by magnetic sorting, are linearly absorbed, with more strictly homogeneous rays, in a

[30] O. von Baeyer and O. Hahn, *Physikal. Zeitsch.*, 1910, **11**, 488 ; *A.*, ii, 566 ; O. Hahn and L. Meitner, *ibid.*, 493 ; *A.*, ii, 566.

[31] In view of the universal use of the symbol λ to express radioactive constants, in future in these Reports the symbol μ will be chosen to express absorption coefficients, according to the custom on the Continent.

[32] J. A. Gray and W. Wilson, *Phil. Mag.*, 1910, [vi], **20**, 870 ; *A.*, ii, 1022.

[33] *Ann. Report*, 1909, 240 ; W. Wilson, *Physikal. Zeitsch.*, 1910, **11**, 101 ; *A.*, ii, 175.

vacuum where no scattering occurs, showed two entirely different cases, according as to whether aluminium or platinum was employed as absorbent. For the first, the curve was neither linear nor exponential, but showed two opposite inflexions, which would, with less refined magnetic sorting, be smoothed out to give a curve apparently linear. Platinum, however, after the first 0·001 cm., for which the curve was very steep, showed for homogeneous β-rays a strictly exponential curve.[34] Again, after passage through 0·001 cm. of platinum, homogeneous β-radiation is exponentially absorbed by aluminium, and the view is taken that exponential absorption is indicative of a completely scattered radiation.[35] The velocity of homogeneous β-radiation is slightly but definitely diminished by passage through aluminium and glass, whilst from platinum the rays emerge with a considerable range of velocity, for the most part, but not altogether, less than initially. The "absorption" of β-rays is, however, due to the complete stopping of a fraction rather than to the retardation of the whole beam. For a heterogeneous β-radiation the velocity of the rays after transmission through an absorbing plate is apparently unaltered, owing to the preferential absorption of the less penetrating rays, whereby the retardation of the transmitted rays is masked, but with homogeneous β-rays the retardation is now well established.[36] The greatest reduction of velocity yet observed is 21 per cent., but owing to the high velocity of the rays and the consequent increase in their apparent mass, this diminution in the velocity corresponds to a reduction of energy of 77 per cent. Over this range the absorption coefficient increased from $4·8(\text{cm.})^{-1}$ to $35·7(\text{cm.})^{-1}$. Thus, although the reduction in velocity is small, the effects produced on the absorption curves are of great importance.

The scattering of homogeneous β-rays was found to bear out a theory of the nature of the action which has been proposed.[37] A deduction from the results was that in all the atoms examined the number of electrons is three times the atomic weight on the view that the positive electricity, assumed to be present, is uniformly distributed, not concentrated in an electronic condition.

The power of different substances to reflect β-rays increases with the velocity of the rays ($H\rho$ from 1000 to 3000), and then diminishes again, although the ratio of the reflecting power of different substances is not influenced by the velocity of the rays.

[34] J. A. Crowther, *Proc. Camb. Phil. Soc.*, 1910, **15**, 442 ; *A.*, ii, 672.
[35] J. A. Crowther, *Proc. Roy. Soc.*, 1910, A, **84**, 226 ; *A.*, ii, 918.
[36] W. Wilson, *ibid.*, 141.
[37] Sir J. J. Thomson, *Proc. Camb. Phil. Soc.*, 1910, **15**, v.

γ-Rays.

The ionisation produced by γ-rays in electroscopes of the same volume is known to vary considerably with the material out of which the electroscope is made, being greatest for lead. Provided that the wall thickness is sufficient to absorb β-rays completely, it has been shown that the relative ionisations in different vessels are a measure of the average ranges of the β-rays generated by the γ-rays in the metals concerned. This method of estimating the average ranges is independent of the amount of deflexion and scattering suffered by the β-ray. In ordinary circumstances, lead absorbs more than other metals, weight for weight, but this is due to the more zigzag character of the path of the β-ray in lead. The average length of the real path of the β-ray, multiplied by the density of the metal, is greatest in lead, although the trajectory is more entangled.[43]

Lead has another advantage in the construction of γ-ray electroscopes, in that it is, of all metals, the least penetrated by the secondary rays generated by the γ-rays in surrounding objects. Provided that a thick lead electroscope is used, with the windows and cork properly screened by lead, the absorption curve of the radium γ-rays in lead is absolutely exponential from 1 cm. to 22 cm., with the value of $\mu(\text{cm.})^{-1}$ 0·50. The departures from the exponential form previously observed, which were supposed to indicate heterogeneity of the rays, are due to secondary rays entering through the sides of the electroscope. The absorption curves over the initial thickness up to 1 cm. of lead, or its equivalent, are not exponential, but the variations are not due to initial heterogeneity of the beam, as the departures are in opposite senses with different metals and different experimental arrangements. With a point source of radium at the centre of a hemispherical ionisation chamber, with absorbing plates in the form of truncated hemispheres, the theoretical absorption curve can be evaluated on the assumption that the γ-rays are homogeneous, and are not scattered. For lead, the curve found agreed closely with the theoretical from the thickness sufficient to absorb β-rays onward, which is strong evidence in favour of the homogeneity of the γ-rays of radium. However, there is other evidence against this view. The phenomenon of the hardening of the γ-rays by passage through increasing thickness of lead, whereby the penetrating power of the transmitted rays towards a lighter metal, such as zinc, is continuously increased, apparently without limit, although the absorption curves are always strictly exponential, is strong evidence in favour of a continuous

[43] W. H. Bragg, *Phil. Mag.*, 1910, [vi], **20**, 385; *A.*, ii, 919

modification of the nature of the γ-radiation by lead. As in the case of the β-rays, the problem arises as to how far a strictly exponential absorption curve is indicative of homogeneity, although it must be remarked that the exponential law holds far more completely for the γ-rays than for the β-rays. The studies before made of the γ-rays of uranium-*X* and radium have now been extended to the two types of γ-rays in the thorium series, from mesothorium-2 and thorium-*D*, and for those of actinium-*C* or -*D*. The general result is to show that the two thorium γ-rays are extremely similar to those of radium-*C* both in penetrating power and in the ratio of the intensity of γ- to β-rays. The γ-rays of thorium-*D* are the most penetrating rays known, being a few per cent. more penetrating than those of radium-*C*, while those of mesothorium-2 are a few per cent. less penetrating. The γ/β ratio of both types is rather less than for radium-*C*, that of thorium-*D* being less than that of mesothorium-2. The γ-rays of actinium are abnormally highly absorbed by lead, and in addition the absorption curve is not exponential, showing two sharp points of inflexion at thickness 0·3 cm. and 0·85 cm., although for other metals the curves are quite exponential. The absorption coefficient is about twice that of radium-*C* for metals other than lead, and varies from seven to three times greater for lead, whilst the γ/β ratio is only from thirteen to eight times as great, according to the method of measurement. In the latter respect therefore actinium is more analogous to uranium than to radium and thorium. All this work emphasises how little connexion there is between the properties of the γ-rays and those of the β-rays which always accompany them, and has strengthened the view that the two types are not interdependent. Indeed, there is far more connexion between the properties of the γ-rays and those of the α-rays which precede and follow them in the disintegration series than with those of the β-rays which accompany them. With the exception of actinium, the more rapid the change, the more penetrating the γ-ray emitted, as is the case for the α-rays.[44]

Secondary γ-*Rays*.—When γ-rays strike a plate of metal, "secondary" γ-rays, softer than the primary, are emitted from both sides of the plate, the "incident" being always softer than the "emergent" secondary rays. The "secondary" rays appear to consist merely of scattered and softened primary rays, and shows no sudden break in properties from the primary, there being a gradual softening the more the secondary radiation departs in direction from that of the primary. The lighter elements produce more secondary radiation than the heavier elements. As the thickness of the

[44] F. and W. M. Soddy and A. S. Russell, *Phil. Mag.*, 1910, [vi], **19**, 725; *A.*, ii, 474; A. S. Russell and F. Soddy, *ibid.*, 1911, [vi], **21**, 130.

plate is increased, both the primary and the emergent secondary rays are hardened. These results have been held to support the view that the primary rays are heterogeneous, the softer radiation being more scattered than the harder, so that the emergent primary beam is hardened by passage through metals.[45] Thus the evidence, as in the case of the β-rays, is conflicting, and much still remains to be explained.

Much interesting work[46] has been done on the homogeneous secondary X-rays. When X-rays fall on a metal, for example, tin, a characteristic secondary "tin" X-radiation is generated, provided that the primary rays possess a sufficient degree of hardness. The degree of hardness necessary increases with the atomic weight of the metal. Characteristic homogeneous secondary X-radiations have so far been obtained from the elements included between iron and antimony, the former being seventy times more easily absorbed than the latter. It does not seem possible to produce a primary X-radiation sufficiently hard to excite the characteristic secondaries of the elements heavier than antimony. The existence of these characteristic radiations explains the great absorbing power of heavy vapours, like ethyl bromide and iodide, for X-rays, which was previously thought to be anomalous, the heavy atoms of the gas being excited to give their characteristic radiation with greatly increased absorption of the primary rays and ionisation in consequence. No such phenomena have so far been observed with γ-rays, and they form, with the polarisation of the X-rays, the two chief arguments in favour of a wave-theory and against the corpuscular theory of the nature of the X-rays. On the other hand, if the argument is confined to the γ-rays alone, the corpuscular theory offers a fairly complete and reasonable view of their properties, and has proved of the greatest service in simplifying the many complex phenomena encountered.[47]

The von Schweidler Variation.—Attempts have been made to settle between the two hypotheses by comparing the von Schweidler variations of the γ-rays due to the irregularity of the individual atomic disintegrations. If the wave-front possesses a heterogeneous structure, as it must have on the corpuscular hypothesis but not on the wave theory, a second von Schweidler variation would be superimposed on the first, which would come the more into evidence

[45] D. C. H. Florance, *Phil. Mag.*, 1910, [vi], **20**, 921.

[46] C. G. Barkla, *ibid.*, 370; *A.*, ii, 920; R. T. Beatty, *Proc. Camb. Phil. Soc.*, 1910, **15**, 416; *A.*, ii, 674; R. D. Kleeman, *Proc. Roy. Soc.*, 1910, A, **84**, 16; *A.*, ii, 567; J. L. Glasson, *Proc. Camb. Phil. Soc.*, 1910, **15**, 437; *A.*, ii, 674; J. C. Chapman and S. H. Piper, *Phil. Mag.*, 1910, [iv], **19**, 897; *A.*, ii, 567.

[47] W. H. Bragg, *Phil. Mag.*, 1910, [vi], **20**, 385; *A.*, ii, 919.

the narrower the pencil of rays employed. A series of experiments on these lines supported strongly the view that the wave front is strongly anisotropic, although, of course, it does not decide whether the rays are propagated along lines or narrow cones.[48] The fact that in all probability the γ-rays do not ionise directly, but by means of the secondary β-rays they generate, and the possibility that in addition to the other variations the number of pairs of ions produced by the individual γ-ray in the gas is also subject to variations of a similar kind, makes the interpretation of such experiments very difficult and uncertain.[49]

Thermo-radioactivity.

The heat evolved by pitchblende, containing 64 per cent. of uranium, has been found to be $6 \cdot 1 \times 10^{-5}$ calories per hour per gram, which is about 30 per cent. higher than the rate calculated from the kinetic energy of the α-particles expelled.[50] With the very sensitive calorimeter before described, the direct heating effect of the α-rays from radium-*C* has been clearly detected, the β- and γ-rays not producing any appreciable action.[51] It has also been established, with the same instrument, that when a phosphorescent salt is mixed with a radium preparation, the same amount of heat is evolved as in its absence, showing that by the intermediate transformation of the energy of the rays into light no alteration is brought about in the amount of heat ultimately produced.[52] By means of a differential air calorimeter of glass, the difference between the heat energy evolved from a zinc sulphide preparation exposed to α-rays, bare and covered with black paper to absorb light, was found to be about 1·5 per cent. of the total heat evolved. This gives a rough estimate of the fraction of the energy of the α-rays converted into light by zinc sulphide.[53]

Radioactive Recoil.

The atomic mass of the recoiled atoms of radium-*B*, which carry positive electric charges, has been determined by the measurement of the electrostatic and electromagnetic deflexion of the atom. The value found for $H\rho$, which is equal to mv/e, in the magnetic deflexion experiment was twice that for the α-particle, indicating,

[48] Edgar Meyer, *Sitzungsber. K. Akad. Wiss. Berlin*, 1910, **32**, 647; *Jahrb. Radioaktiv. Elektronik*, 1910, **7**, 279; *A.*, ii, 673.

[49] E. von Schweidler, *Physikal. Zeitsch.*, 1910, **11**, 225, 614; *A.*, ii, 376, 766.

[50] H. H. Poole, *Phil. Mag.*, 1910, [vi], **19**, 314; *A.*, ii, 176.

[51] *Ann. Report*, 1909, 245; W. Duane, *Compt. rend.*, 1910, **151**, 471; *A.*, ii, 815.

[52] W. Duane, *Compt. rend.*, 1910, **151**, 379; *A.*, ii, 816.

[53] E. Marsden, *Proc. Roy. Soc.*, 1910, A, **83**, 548; *A.*, ii, 565.

since the momentum mv of the recoiling atom must be equal to that of the α-particle, that the recoiling atom carries a single positive charge. From the combined deflexions, the velocity of the recoiling atom was found to be $3{\cdot}23 \times 10^7$ cm. per second, and its mass, 194 ($H = 1$). The difference between the latter number and the value 214·5, calculated by subtracting from the atomic weight of radium three times that of helium, is not significant, as the experiments do not permit of a high degree of accuracy.[54]

The amount of product recoiled in an α-ray change, for example, radium-A from the emanation, or radium-B from radium-A, is much greater than the amount in a β-ray change, for example, radium-C_2 from radium-C_1, as is to expected. But it seems that even in a rayless change, or one in which only a very feeble β-ray is expelled, as that of radium-B, a perceptible amount of the product (radium-C_1) is recoiled, which varies capriciously in different experiments. The recoiling radium-C_1 atom, which carried no charge, possesses a penetrating power about one-fortieth of that of the recoiled radium-B atom. It is probable that in this case mechanical disturbance, due to the violent disintegration of radium-C, brings about the projection of neighbouring radium-C atoms, as the energy they possess is far greater than is to be expected if they were really recoiled during the disintegration of radium-B.[55]

Some evidence has also been obtained that recoiled atoms of radium-B can be scattered by a reflector and deposited on a surface out of the direct line of fire of the stream, but the possibility that atoms can be mechanically removed by the disintegration of neighbouring atoms, so simulating a recoil phenomenon, makes the interpretation of the results difficult.[56]

The range of radium-B recoiling from radium-A is about 400 times less than that of the α-particles of radium-A, or about a tenth of a millimetre of air at normal pressure. A single gold leaf, of 0·08 μ thickness, would thus completely stop the recoiled atoms. In hydrogen the range is about six times that in air. Some interesting experiments were done with plates which, after immersion in the emanation, were silvered to different extents. A coating of silver 20 $\mu\mu$ in thickness stopped the recoil completely, while 10 $\mu\mu$ allowed some 60 per cent. of the recoiling atoms to pass through. In the distribution upon surfaces of the active deposit from the emanation, recoil phenomena play an important part,

[54] S. Russ and W. Makower, *Phil. Mag.*, 1909, [vi], **20**, 875; W. Makower and E. J. Evans, *ibid.*, 882; *A.*, ii, 1022, 1023.

[55] W. Makower and S. Russ, *ibid.*, 1910, [vi], **19**, 100; *A.*, ii, 91; S. Russ, *Le Radium*, 1910, **7**, 93; *Mem. Manchester Phil. Soc.*, 1910, **54**, No. viii, 1; *A.*, ii, 475.

[56] W. Makower and S. Russ, *Mem. Manchester Phil. Soc.*, 1910, **55**, No. i, 1.

especially in gas at low pressure. In the case of radium-D, which, owing to its extended life period, possesses a radioactivity too feeble to be detected in ordinary circumstances, there is some evidence that it may be possible to follow its recoil from radium-C_2 by means of the ionisation the projected particles produce in a gas at low pressure.[57]

Influence of Temperature on Radioactive Change.

Many of the effects which were supposed to indicate an alteration in the rate of change in the active deposit of radium at high temperature have received a satisfactory elucidation, and the question may now be considered settled. The hard γ-rays show practically no change when, for example, a radium preparation in a quartz tube is heated in an electric oven to 1200° to 1300°, either during the heating or subsequently. But the β-rays show a curious and complex sequence of variations, which are such as can be accounted for by changes in their absorption by the preparation itself. The first effect of the heating is to liberate the occluded emanation and to gasify the products radium-A, -B, and -C from the preparation, causing a lessened absorption and consequent sudden increase of β-radiation. On cooling, the products, all except the emanation, are suddenly absorbed again by the preparation, with a consequent sudden return of the β-radiation to its initial value. Three hours afterwards, a new set of products is produced on the walls of the containing tube from the liberated emanation, which causes the β-radiation gradually to return to its higher value. Then over a period of three weeks, the liberated emanation decays, while fresh is produced within the solid preparation, producing a gradual decay of the β-rays to their initial value. The conclusion is that so far as experiments have yet been carried, temperature produces no real change in the rate of atomic transformation.[58]

The Uranium-Radium Disintegration Series.

A series of measurements, giving the relative proportion of β-rays contributed by the different constituents of uraninite in a cylindrical electroscope 40 cm. high and 40 cm. diameter, gave as the result that uranium-X (hard rays only) contributes about one-third, radium-B and -C about one-half, and radium-E about 10 per cent.[59]

Uranium-X.—A new determination of the radioactive constant of uranium-X gave a result about 10 per cent. less than the value

57 L. Wertenstein, *Compt. rend.*, 1910, **150**, 869 ; **151**, 469 ; *A.*, ii, 476, 816.
58 H. W. Schmidt and P. Cermack, *Physikal. Zeitsch.*, 1910, **11**, 793 ; *A.*, ii, 918.
59 S. J. Lloyd, *J. Physical Chem.*, 1910, **14**, 509 ; *A.*, ii, 765.

previously used, namely, $0·0282(\text{day})^{-1}$. This makes the period of average life 35·5 days, and that of half-change 24·6 days. The values obtained from the decay curves of the γ- and β-rays, the first over a period of eight months and the second over fourteen months, were identical, both types of rays decaying normally to zero. The uranium-X was prepared from 50 kilos. of uranium nitrate, and the observations of the γ-rays were continued until they were reduced to about 1/700th, and of the β-rays to 1/100,000th of their initial value.[60] The further study of these and similar preparations to determine whether a feeble α-radiation developed as the β-radiation decayed, either concomitantly or subsequently, as is to be expected if ionium is the product of the disintegration, has given a completely negative result. A feeble constant α-radiation remains after the penetrating radiation has completely decayed, but it is present from the start, and is due to impurities separated from the uranium. The conclusion from these experiments is that, if ionium is the direct product of uranium-X, its period of average life must be greater than 35,000 years as a minimum, which agrees with the experiments on the absence of growth of radium in uranium solutions (p. 275). Neither has any indication of the growth of actinium from these preparations yet been obtained, but actinium in minute amount is present from the start as an impurity.[61]

Evidence has been obtained in the adsorption of uranium-X, by precipitating barium sulphate in a solution of uranium nitrate, of the existence of a definite partition coefficient between the absorbent and the solution. Experiments carried out by precipitating different amounts of barium sulphate in similar solutions under exactly the same conditions showed that the distribution obeys the law $c/C^n = \text{constant}$, where c and C are the concentrations of the uranium-X in the solid and liquid phases respectively, and n is a constant. This relation probably only holds for the initial distribution immediately after precipitation, as, no doubt, on keeping, the uranium-X would diffuse into the barium sulphate particles, lessening the surface concentration, and enabling the barium sulphate to withdraw further amounts of uranium-X from the solution.[62]

The following method of separating uranium-X from uranium nitrate has been recommended. Soot, freshly obtained by burning naphthalene, is stirred into the acetone solution, and then extracted with hydrochloric acid. Iron is added to the extract, and precipitated with ammonium carbonate in excess. The uranium-X is

[60] F. Soddy and A. S. Russell, *Phil. Mag.*, 1910, [vi] **19**, 847; *A.*, ii, 568.
[61] F. Soddy, *ibid.*, **20**, 342; *A.*, ii, 921.
[62] A. J. Berry, *Trans.*, 1910, **97**, 196.

freed from the iron precipitate by dissolving it in concentrated hydrochloric acid, and extracting the solution with freshly distilled ether saturated with hydrogen chloride, when the uranium-*X* remains dissolved in the aqueous layer.[63]

The statement occurs in various places that uranium-*X* and thorium are chemically analogous and cannot be separated, but no detailed researches have been published.[64] This would explain at once the remarkable fact commented on last year,[65] that a trace of thorium sulphate added to a uranium solution completely prevents the adsorption of uranium-*X* therefrom by means of charcoal. It has been noticed that the short-lived radioactive products are much more prone to separation by adsorption than the long-lived. The reason for this is clear, since when quantities of different radioactive products of similar intensity of radioactivity are compared, as is usually the case, these quantities are proportional to the periods of the products. If, now, a given quantity of an adsorbent is able to absorb the same absolute quantity of two different radioactive products, the adsorption may be practically complete for the one product if it is short-lived; and inappreciable for the other if it is long-lived, although the actual masses of each adsorbed is the same. If there is also present an element either not radioactive, or, if radioactive, of long period, which has a chemical nature entirely analogous to that of the short-lived product, it follows that a mere trace of it will be sufficient entirely to stop the adsorption of the short-lived product.[66]

The Relation between Uranium and Radium: Ionium.—The rate of growth of radium in the purified uranium solutions, which was before stated to have increased during the fourth year from preparation, according to the square of the time, has not been maintained. There was an undetected error in the measurements. It is probable that the undoubted growth of radium, so far observed, is due to a trace of ionium initially present, and that the growth from uranium has not yet appreciably started. This increases the minimum estimate of the period of average life of ionium to at least 35,000 years, if there is only one long-lived intermediate body in the series, and the extended period is in agreement with the experiments on the absence of a growth of α-radiation from uranium-*X* already described.[67] The variations

[63] S. J. Lloyd, *J. Physical Chem.*, 1910, **14**, 509 ; *A.*, ii, 765.

[64] B. Keetman, *Jahrb. Radioaktiv. Elektronik*, 1909, **6**, 265 ; *A.*, 1909, ii, 852 ; W. Marckwald, *Ber.*, 1910, **43**, 3421 ; *A.*, 1911, ii, 8.

[65] *Ann. Report*, 1909, 262.

[66] F. Soddy, *Trans.*, 1911, **99**, 72.

[67] *Ann. Report*, 1909, 262 ; F. Soddy, *Phil. Mag.*, 1910, [vi], **20**, 340 ; *A.*, ii, 921.

in the uranium-radium ratio in autunite and thorianite have been re-examined.[68] Some of the results with Portuguese autunite have been referred to under *Helium* (p. 263). Various specimens examined showed a radium ratio from 70 to 44 per cent. of the equilibrium ratio, whilst a specimen from Autun, France, had only 27 per cent., the lowest yet recorded. The ratio for thorianite was found to be only slightly greater than that for Joachimsthal pitchblende. It is probable that the extended life period of ionium will account for all these departures, and that even in Joachimsthal pitchblende the radium ratio may be slightly lower than the true equilibrium ratio, owing to the mineral not being sufficiently old. The small amount of helium in this mineral is evidence that it must be, geologically, a recent formation.

It is interesting to note that the exact law of radioactive equilibrium is $\lambda_N x_N = \lambda_A(x_A + x_B + x_C + \ldots x_N)$, where x_A, x_B, x_C, etc. are the quantities of the successive members of a disintegration series, and λ_A, λ_B, λ_C, etc., their radioactive constants.[69]

This relation becomes identical with the usual approximate relation $\lambda_N x_N = \lambda_A x_A$ when the periods of the products are negligible by comparison with that of the parent element. It shows that even were the period of ionium a million years, its effect on the equilibrium ratio of radium to uranium would be less than a tenth per cent.

In a very complete chemical investigation of the "hydrate" fraction obtained from the working up of ten tons of Joachimsthal pitchblende for radium, which contained the actinium and ionium of the mineral together with rare-earths, the ionium followed all the reactions of thorium, and was separated with this element from all the other constituents. For details, the original work must be consulted. Numerous fresh attempts to separate the ionium from thorium, including various fractionation processes and the heating of the oxide in the electric arc, failed completely in their purpose, as have many independent attempts previously.[70]

Actinium.—In the same research, actinium, which is known to follow the reactions of lanthanum very closely, was found to stand chemically between lanthanum and calcium. It was observed that in presence of ammonium salts neither ammonia nor ammonium oxalate precipitate actinium completely, but in presence of manganese it can be precipitated from the basic solution as a

[68] *Ann. Report*, 1909, 260; F. Soddy and Miss R. Pirret, *Phil. Mag.*, 1910, [vi], **20**, 345; *A.*, ii, 922; A. S. Russell, *Nature*, 1910, **84**, 238; compare Mme. Curie, *Radioactivité*, II, 441.

[69] H. Mitchell, *Phil. Mag.*, 1911, [vi], **21**, 40.

[70] C. Auer von Welsbach, *Sitzungsber. K. Akad. Wiss. Wien*, 1910, **119**, [iia], 1; *A.*, 1911, ii, 7.

manganate, which proved to be a reaction of great value in its separation. This piece of work was carried through without recourse to the usual method of adding the element most nearly allied chemically to the radioactive substance and then separating them together, in order the more completely to elucidate the chemical nature of the extremely complicated mixtures treated. Indications of new non-radioactive elements were obtained.

Actinium-B.—Further evidence of the dual character of this product, shown by the slight difference of range of the α-particles emitted, has been obtained, the most important being that the scintillations, examined in a gas over the range of increasing pressure necessary to cause the α-particles just not to reach the screen, disappear less abruptly than in the case of a substance like polonium, known to give a homogeneous set of α-particles.[71]

Radium.—Foremost in the work on radium is its isolation in the elementary state as metal. About one-tenth of a gram of perfectly pure radium chloride was electrolysed with a mercury cathode until the solution contained less than 10 per cent. of the initial radium. The amalgam of radium, which was fluid, whereas parallel experiments with barium chloride had given a partly solid amalgam, was dried and cautiously ignited in an iron boat in a current of specially purified hydrogen at reduced pressure. When the temperature reached 400°, the amalgam became solid. At 700° no more mercury volatilised, and the boat contained a brilliant white metal, which melted sharply at about 700°, volatilising appreciably at the same temperature. Thus, in volatility and fusibility, radium resembles calcium rather than the much less fusible and volatile barium, and it is possible that sublimation in a vacuum may serve to separate radium from barium. Radium behaved as is to be expected of an alkaline-earth metal, dissolving in water with energetic evolution of hydrogen, and tarnishing rapidly in the air with the formation, probably, of the nitride. Its radioactive behaviour was also normal, the penetrating radiation from the metal, sealed in a glass tube, being generated according to the law of the production of the emanation.[72] Another interesting attempt to isolate radium from a mixture of the barium and radium azoimides, by careful heating in a "melting-point tube" to 185—250° in a perfect vacuum, yielded a shining, metallic mirror, containing the greater part of the radium employed, which behaved in the same way as metallic barium, appearing to form the nitride in moist air with even greater readiness.[73] These

[71] Mlle. L. Blanquies, *Compt. rend.*, 1910, **151**, 57; *Le Radium*, 1910, **7**, 159; *A.*, ii, 768.

[72] Mme. Curie and A. Debierne, *ibid.*, 523; *A.*, ii, 816.

[73] E. Ebler, *Ber.*, 1910, **43**, 2613; *A.*, ii, 1024.

advances bring to a fitting consummation the long series of researches which began with the recognition of radium as a new member of the alkaline-earth family of elements, but, as was to be expected, do not add anything new on the radioactive side, for the existence of all the radioactive properties of uranium unmodified in the metallic state has long been known.

A careful estimation of the radium in all the by-products from the extraction of radium from 10 tons of Joachimsthal pitchblende, showed that there was present in all only 0·26 gram, of which two-thirds was present in the unattacked residue from the soda extractions, and about one-quarter in the lead products.[74]

Radium Emanation.—Bunsen's method of determination of the density of a gas, by its velocity of escape from a small hole in a thin partition, has been applied to radium emanation, mixed with from 5 to 200 times its volume of foreign gas at a pressure of about 0·01 mm. of mercury, the vessel into which the gas escaped being kept continuously exhausted by a rotary mercury pump. With a mixture of argon and oxygen under these conditions, each gas behaved as if alone present at its partial pressure, and for the emanation the amount of foreign gas present exerted no influence on its rate of escape. The results, compared with those obtained with argon and oxygen, gave a value for the molecular weight of the emanation of about 220, the experiments not varying more than 2 or 3 per cent.[75]

The density of the emanation has been determined directly by means of the quartz micro-balance before described.[76] Although the quantities of emanation employed were almost infinitesimal, in no case exceeding 0·1 cu.mm. volume at atmospheric pressure, and of weight of the order of one-half a micro-gram, consistent results were obtained for the molecular weight of the emanation, lying between 216 and 228, with a mean value 220. The volume of the emanation was calculated from the volume in equilibrium with 1 gram of radium (0·601 cu.mm.) previously found.[77] Both of these results and that already given on the molecular weight of radium-*B* (p. 272) bear out fully the method of calculating the atomic weights of the members of the uranium-radium disintegration series by the subtraction from the atomic weight of uranium or of radium the known number of helium atoms expelled in their formation.

A new determination of the period of the emanation, both by means of the β- and γ-rays from a quantity in a sealed tube, and

[74] Helene Souczek, *Sitzungsber. K. Akad. Wiss. Wien*, 1910, **119**, [ii*a*], 371.

[75] A. Debierne, *Compt. rend.*, 1910, **150**, 1740; *A.*, ii, 675.

[76] *Ann. Report*, 1909, 267.

[77] Sir W. Ramsay and R. W. Gray, *Compt. rend.*, 1910, **151**, 126; *A.*, ii, 767.

by means of the α-rays, the emanation being enclosed in an air-tight ionisation vessel, gave, in five determinations by each method, results consistent to 1 per cent. The period of average life is 5·55 days, and of half-change, 3·85 days. The radioactive constant, $\lambda(\text{hour})^{-1}$, is 0·00751. In these experiments, the concentration varied over a range of 2×10^{11}. In single experiments, the exponential decay continued for three months, over a decay to one ten-millionth of the initial quantity, so that no more complete proof could be desired of the absolute independence of the rate of radioactive change upon concentration.

Among other investigations of interest in connexion with the use of the emanation in the estimation of radium,[78] some results have been obtained which throw light on the progressively diminishing rate of production of emanation from a solution in which the radium has been freshly precipitated, which has raised the question whether an intermediate body, "radium-*X*," exists in the series. Heating a solution in which the rate of production had diminished with time, enormously increased the amount of emanation evolved, showing that the emanation was generated as usual, but accumulated in, and was not evolved from, the cold liquid. This is ascribed to the slow formation of an invisible precipitate of non-emanating radium sulphate, which re-dissolves when the solution is heated.[79] The formation of other precipitates in a solution containing radium and barium does not much affect the amount of emanation evolved, but sodium carbonate and sulphuric acid cause a notable diminution, due to the precipitation of the radium. Stirring and heating a solution in which radium and barium sulphate have been precipitated causes the radium again to go into solution, so that a radium solution after barium sulphate has been precipitated in it, but not removed, may recover its initial power of evolving emanation.[80]

Experiments on the release of emanation from various salts containing radium by heating have shown that the same fraction is retained whether the salt is maintained at the high temperature or heated to it for only a short time before the extraction. This fraction, which is a function of the temperature only, not of the time of accumulation, is constant for any given preparation, but varies widely with different preparations, being less for impure preparations than for those containing barium and radium only. With minute quantities of pure radium chloride, it was found that the material was chemically changed by the heating, becoming

[78] W. Duane and A. Laborde, *Compt. rend.*, 1910, **150**, 1421 ; *Le Radium*, 1910, **7**, 162 ; *A.*, ii, 676 ; Mme. Curie, *Le Radium*, 1910, **7**, 65 ; *A.*, ii, 476.

[79] L. Kolowrat, *Le Radium*, 1910, **7**, 157.

[80] S. J. Lloyd, *J. Physical Chem.*, 1910, **14**, 476 ; *A.*, ii, 568.

insoluble and no longer evolving its emanation completely at the fusion temperature.[81]

The absorption of the emanation by cocoanut charcoal, in this method of estimating the amount in the atmosphere, is never complete, but the fraction absorbed was found to be the same for solutions of different amounts of radium, up to 6×10^{-9} gram. The fraction absorbed diminishes as the velocity of the air stream increases and with the time the experiment lasts, as though the charcoal became superficially saturated.[82] Other experiments have not confirmed the great difference found in the temperature of volatilisation of the condensed emanation from glass and metal surfaces respectively.[83] In this new work, almost inappreciable differences, not greater than 4°, were observed.[84]

Radium-D.—Numerous attempts have been made to concentrate radium-*D* (radio-lead) from lead, but without success,[85] and there is good reason for thinking that the two elements form a non-separable pair, of which so many cases now exist. The separation would be a valuable one, if it were possible, as all the β-rays of the mineral due to the radium-*E* are at present not utilised, the lead separated having a β-activity not very much greater than uranium. However, pure radium-*D* can be formed in minute amount from the radium emanation by leaving it to decay in a sealed tube. In course of time this develops polonium or radium-*F*, which gives α-particles. By counting the number of scintillations produced by the α-particles emitted after a known time from a known initial quantity of the radium emanation, the period of radium-*D* can be determined. Five results by this method gave the result 16·5 years ($\pm$0·5 year) for the period of half-change. In the course of this work, it was found that a quantity of radium-*D* deposited during a single day from a large quantity of the emanation developed the β-radiation due to radium-*E* regularly and normally with the half-change period of five days. When radium-*E* is separated from a solution of radium-*D* by precipitating the latter with barium sulphate, the β-rays decay normally with the same period. These results disprove the existence of an intermediate rayless product, radium-E_1, in the series. Only one product, radium-*E*, exists between radium-*D* and polonium, and this gives β-rays, and has a period of half-change of 5·0 days. Radium-*D* is removed with radium from an old radium preparation

[81] L. Kolowrat, *Le Radium*, 1909, **6**, 321 ; **7**, 266 ; *A.*, ii, 91, 1023.

[82] J. Satterley, *Phil. Mag.*, 1910, [vi], **20**, 778 ; *A.*, ii, 921.

[83] *Ann. Report*, 1909, 254.

[84] R. W. Boyle, *Phil. Mag.*, 1910, [vi], **20**, 955 ; *A.*, 1911, ii, 6.

[85] H. Herschfinkel, *Le Radium*, 1910, **7**, 198 ; *A.*, ii, 817.

by the precipitation of barium sulphate, leaving radium-*E* and polonium in solution.[86]

Polonium.—In the working up of some tons of residues of uranium minerals, the polonium was obtained in a final concentrated product, weighing 2 milligrams. It was estimated that the actual quantity of polonium present was 5 per cent. of this weight, and corresponded with the amount in about 2 tons of good pitchblende. The product gave a spectrum showing several new lines, and it is proposed to see if these alter in intensity and disappear from the spectrum as the polonium disintegrates. By the same tests it is hoped to see whether the spectrum of lead, which, although not altogether absent in the preparation initially, was very feeble, increases in intensity as the polonium decays. In the course of a year or two the greater part of the polonium will have disintegrated, and the results of the subsequent spectroscopic investigation will be awaited with interest.[87] Old polonium preparations decay regularly and completely with the normal period, showing that no further products possessing detectable activity exist.[88] There can be little doubt that the product will prove to be lead. What the end products of the thorium and actinium series are there is at present no means even of guessing.

The Thorium Series.

Mesothorium.—Preparations of mesothorium more concentrated than pure radium salts, as regards the intensity of the penetrating rays, have, during the year, been prepared by a secret process from monazite sand and put on the market. The period of average life of the parent substance, mesothorium-1, is about 8 years, and during the first two years, through the growth of radiothorium, the initial penetrating radiation is about doubled before the decay commences. The substance then possesses the whole of the radioactivity of the thorium series in concentrated form, with the exception of a few per cent. of low range α-rays. It produces the whole of the penetrating rays, the thorium emanation, and active deposit, corresponding with the thorium series in the mineral from which it was extracted. Although not a permanently radioactive substance, the useful life is sufficiently long to make it worth extracting, especially as it is merely a by-product of the thorium industry, which consumes annually an enormous amount of the raw material, monazite sand. Although the nature of the manu-

[86] G. N. Antonoff, *Phil. Mag.*, 1910, [vi], **19**, 825 ; *A.*, ii, 568.
[87] Mme. Curie and A. Debierne, *Compt. rend.*, 1910, **150**, 386 ; *A.*, ii, 251.
[88] J. W. Waters, *Phil. Mag.*, 1910, [vi], **19**, 905 ; *A.*, ii, 569.

facture of mesothorium preparations has been kept entirely secret, two separate investigations of the chemical nature of the substance have established the interesting fact that it is absolutely identical in all its reactions with radium.[89] In the ordinary technical treatment of monazite sand, by heating it with excess of sulphuric acid and stirring the product with water, part of the mesothorium remains with the insoluble residue, and part passes into solution, from which it may be removed by a barium sulphate precipitation. If, however, a barium compound in small quantity is added to the monazite sand before treatment, the whole of the mesothorium is contained in the insoluble residue. From the latter, or, indeed, from any mixture containing it, it may be recovered by processes identical in every respect to those in use in the working up of radium residues. A long series of fractionations of barium chloride, containing mesothorium and radium, concentrated the two radioactive substances together from the inactive barium chloride without changing their relative proportions in the slightest degree. The rapidly changing product, thorium-*X*, is always separated with the mesothorium and radium from minerals, and these three substances form a trio of chemically non-separable radio-elements. The possibility of accidental or intentional adulteration of radium with mesothorium must be borne in mind in view of the identity of their chemical properties and great similarity of their penetrating rays (p. 269). A simple test is, after heating or dissolving the preparation to remove radium emanation and resealing the preparation, to take the intensity of the penetrating rays three hours afterwards, when the activity is due to mesothorium alone, and three weeks later, when the full activity due to radium is also present. The ratio of these two measurements gives the proportion of mesothorium present. A careful measurement of the absorption coefficient of the γ-rays will also serve to reveal the presence of mesothorium, the γ-rays of which are rather less penetrating than those of radium, and this test does not require the tube to be opened. For a mixture of the two substances, instead of an exponential absorption curve with constant value of μ from 1 cm. of lead onward, the value of μ will decrease for the first few cm. until the value for radium is attained.[90] Since thorium minerals always contain more or less uranium, mesothorium free from radium has not yet been prepared.

Thorium-D.—Electrolysis for a few seconds of the solution of the active deposit of thorium in concentrated hydrochloric acid (0·5 milliamperes with platinum electrodes $0{\cdot}5 \times 2{\cdot}1$ cm., 1 cm. apart)

[89] W. Marckwald, *Ber.*, 1910, **43**, 3420; *A.*, 1911, ii, 8; F. Soddy, *Trans.*, 1911, **99**, 72.

[90] A. S. Russell and F. Soddy, *Phil. Mag.*, 1911, [vi], **21**, 130.

separates pure thorium-*B* on the cathode, the α-rays of which decay normally with the sixty minutes half-period, but the β-rays of which rise from zero to a maximum with the 3·05 minutes half-period of thorium-*D*. Nickel shaken in the solution withdraws pure thorium-*B* as in the electrolysis. In these respects, thorium-*D* is an exception to von Lerch's rule, that in a disintegration series the successive products are progressively more "noble" in their electrochemical behaviour, thorium-*D* being less "noble" than thorium-*B*. Thorium-*D* is also more easily volatilised than the other products of the active deposit, being completely removed from a wire by thirty seconds' heating in a Bunsen flame, and it is also less soluble in acids.[91]

Radioactivity of Rocks and Minerals.

The rocks from the transandine tunnel proved to be low in radioactive constituents, both thorium and radium, in agreement with the absence of abnormal temperature gradients encountered during the piercing of the tunnel.[92] Calcareous and dolomitic rocks of various origins proved to be very poor in thorium. It is probable that the element is selectively rejected by the organisms in sea water which abstract lime. But sedimentary rocks almost always contain an easily detected quantity of thorium, 1·3 and 0·6 ($\times 10^{-5}$ gram of thorium per gram) being average values for the argillaceous and arenaceous group respectively. It is probable that in these rocks the thorium has been concentrated owing to the removal by gravity before deposition of the larger particles of felspar and quartz.[93] Ten rocks from the west coast of Sumatra contained amounts of radium of the order of 10^{-12} gram per gram, which were very similar to the amounts found for rocks from Europe and America.[94]

A new Australian mineral, named pilbarite, after the locality where it is found, occurs in nodules, up to 30 grams in weight, of amorphous, colloidal, gelatinous or gummy texture, the interior bright canary colour being disguised by a superficial brown or red coating. It is a hydrated silicate of thorium, uranium, and lead, probably being a hydrous pseudomorph of an anhydrous parent mineral, and is soluble in strong acids, leaving silica. Analysis: $UO_3 = 27·09$; $ThO_2 = 31·4$; $PbO = 17·26$; $SiO_2 = 12·72$;

[91] F. von Lerch and E. von Wartberg, *Sitzungsber. K. Akad. Wiss. Wien*, 1909, **118**, [ii*a*], 1575.

[92] A. L. Fletcher, *Phil. Mag.*, 1910, [vi], **20**, 36; *A.*, ii, 677.

[93] J. Joly, *ibid.*, 125, 353; *A.*, ii, 723, 969.

[94] E. H. Büchner, *Proc. K. Akad. Wetensch. Amsterdam*, 1910, **13**, 359; *A.*, ii, 1025.

$H_2O = 7{\cdot}56$ per cent.[95] A find of another radioactive mineral in the interior of South Australia is also reported in the Press.

Atmospheric and Natural Radioactivity.

The examination of spas and thermal springs, and waters in general in all parts of the world proceeds apace on account of the supposed medicinal value of the dissolved radium emanation, but no essentially new facts have transpired. A very complete examination of the radioactivity of the hot springs of Iceland[96] failed to throw any definite light on the nature of hot springs or to establish any direct connexion between the radioactivity and the heat energy. The springs contained on the whole about the same amounts of radium emanation as the mineral springs of Germany and Austria, although none were found quite so active as the most active of these. The absence of any appreciable amounts of radium in the sediments and deposits around the springs is considered a strong argument in favour of the theory that the spring water is heated by steam, as otherwise it is to be expected that these deposits would contain radium derived from the rocks of the interior.

Numerous investigations have also been made of atmospheric radioactivity.[97] Specially interesting are the tests made at the Sestola Observatory in the Apennines, over 3000 feet high, and exposed to all the four winds. The proportion of the activity, obtained by four hours' exposure of a charged wire, due to thorium varied from 29 to 73 per cent., being increased by falling barometer and high winds.[98] The average amount of radium emanation in the air at Cambridge, England, was found to be 1·7 molecules per c.c., and varied over a range of three times greater and three times less than this figure, according, chiefly, as to whether the prevailing wind had passed over the land or ocean previously. The ions produced by the average amount of emanation are 2·1 per c.c. per second. It is estimated that in the free air the thorium emanation produced a similar number, whilst only 1 is produced by the penetrating rays from the earth. In closed vessels the latter number may be increased fourfold.[99]

95 *Australian Mining Standard*, 7/9/10.

96 T. Thorkelsson, *Mémoires de l'Acad. Royale des Sciences et des Lettres de Danemark, Copenhague*, 1910, [vii], **8**, 182; *A.*, 1911, ii, 9.

97 K. Kurz, *Abh. K. Akad. Wiss. München*, 1909, **25**, 5; *A.*, ii, 476; A. S. Eve, *Phil. Mag.*, 1910, [vi], **19**, 657; *A.*, ii, 479.

98 D. Pacini, *Physikal. Zeitsch.*, 1910, **11**, 227; *A.*, ii, 374.

99 J. Satterley, *Phil. Mag.*, 1910, [vi], **20**, 1; *A.*, ii, 676.

Chemical Relationships of the Radio-elements.

A method of determining the chemical nature of a member of a disintegration series by isomorphism consists in adding varying salts to the solution, allowing them partly to crystallise out, and determining which kinds of salts crystallise with the active material. Thus, when barium nitrate or chloride or lead nitrate crystallises in a thorium-*X* solution, the crystals are very active, whereas crystals of potassium, bismuth, or lanthanum ammonium nitrate so formed are inactive. In this way, it has been found that thorium-*X*, actinium-*X*, and radium show a complete identity of chemical behaviour, and are members of the alkaline-earth group of elements.[1] To this group, as already described, mesothorium-1 also belongs, whilst another chemically identical group comprises thorium, radiothorium, radioactinium, ionium, and uranium-*X*. The three emanations form a similar group, and, working backward from them through the three disintegration series, the preceding members, radium, thorium-*X*, and actinium-*X*, are identical chemically and belong to the alkaline-earth family, whilst before these come ionium, radiothorium, and radioactinium, chemically identical with one another and with thorium. These regularities [2] may prove to be the beginning of some embracing generalisation, which will throw light, not only on radioactive processes, but on the elements in general and the Periodic Law. Of course, the evidence of chemical identity is not of equal weight for all the preceding cases, but the complete identity of ionium, thorium, and radiothorium, of radium and mesothorium-1, and of lead and radium-*D*, may be considered thoroughly well established. Indeed, when it is considered what a powerful means radioactive methods of measurement afford for detecting the least change in the concentration of a pair of active substances, and the completeness and persistence of some of the attempts at separation which have been made, the conclusion is scarcely to be resisted that we have in these examples no mere chemical analogues, but chemical identities. The atomic weight of the members in these groups cannot be the same. For example, that of ionium must be 230·5, of thorium 232·5, and of radiothorium 228·5. Radium-*D* must be four units higher than lead; whilst radium, 226·5, mesothorium-1, 228·5, and thorium-*X*, 224·5, are like the first group, two units separating the consecutive members. On the other hand,

[1] D. Strömholm and T. Svedberg, *Zeitsch. anorg. Chem.*, 1909, **61**, 338; **63**, 197; *A.*, 1909, ii, 200, 849.

[2] Compare also O. Hahn and L. Meitner, *Physikal. Zeitsch.*, 1910, **11**, 493; *A.*, ii, 566.

some members which presumably have identical atomic weight belong to different families, as mesothorium-1 and radiothorium, radium-*D* and polonium. The recognition that elements of different atomic weight may possess identical chemical properties seems destined tó have its most important application in the region of inactive elements, where the absence of a second radioactive nature, totally unconnected with the chemical nature, makes it impossible for chemical identities to be individually detected. Chemical homogeneity is no longer a guarantee that any supposed element is not a mixture of several of different atomic weights, or that any atomic weight is not merely a mean number. The constancy of atomic weight, whatever the source of the material, is not a complete proof of homogeneity, for, as in the radio-elements, genetic relationships might have resulted in an initial constancy of proportion between the several individuals, which no subsequent natural or artificial chemical process would be able to disturb. If this is the case, the absence of simple numerical relationships between the atomic weights becomes a matter of course rather than one for surprise.

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